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Separation of Quinoline and Iso-Quinoline by Column Chromatography and their Estimation by Conductivity Measurement

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A new method for the separation of quinoline and iso-quinoline in quantitative yield has been worked out by a column chromatographic technique using silica gel of 200 mesh (B.S.) with 1.7 pH hydrochloric acid and benzene as the stationary and mobile phases respectively. The estimation of the separated fractions has been done by conductivity measurement. The method of estimation was found to be applicable in the range of concentration from 0 to 0.140 per cent w/v for quinoline and 0 to 0.122 per cent w/v for iso-quinoline in a N/50 hydrochloric acid solution.

Quinoline and iso-quinoline and their derivatives are important raw materials for the preparation of dyes and drugs. These are generally recovered from coal-tar distillate, boiling in the range 235-245°C, which is the main source for higher boiling tar bases. The coke oven ammoniacal liquor is the principal source of low boiling tar bases viz. pyridines, picolines and lutidines.

In order to carry out the recovery processes it is essential to first determine the total composition of the bases present therein. An ultraviolet spectrophotometric method for determining the total pyridines and quinolines in high temperature carbonization liquor of Sindri coke oven plant has been developed by the present authors[1]. The separation of quinoline and iso-quinoline cannot be effected by fractional distillation as their boiling points are very close, viz. 237.3 and 242.5°C respectively, and the isolation of quinoline is rendered more difficult by the fact that in fractional distillation not only quinoline but its methyl substituted bases are also carried over. In view of the above difficulties the separation of quinoline and iso-quinoline in quantitative yield has been a subject of scientific investigation during the past few years[2,3]. It was, therefore, thought desirable to investigate into this separation by the application of partition column chromatography, which has proved of immense help in resolving closely resembling fractions in recent years[4,5].

Experimental

The separation of quinoline and iso-quinoline by the classical adsorption chromatographic technique was carried out but was found unsuitable for its inherent difficulties due to the non-linearity of adsorption isotherm and deactivation of the active adsorbent material used as column packing and because it required a large volume of solvents for complete elution. Considering that liquid-liquid partition chromatography is a valuable analytical tool for the compounds which decompose or are difficult to separate in gas-liquid chromatography[6], the same has been adopted in this separation. The available literature shows that separation of these compounds has not been studied so far by liquid-liquid column partition chromatography. Based on this technique a new process has now been developed for separating these bases into their individual components.

Silica gel of 200 mesh (B.S.) E. Merck, hydrochloric acid A.R. (B.C.P.W.), Benzene crystallisable G.R. Sarabhai Merck were used in the preparation of the column.

Column Preparation and Packing: 25 g. of silica gel, the solid inert support for the stationary phase was

activated for 3 to 4 hours at 110°C and kept in a desiccator to cool down to room temperature. The activated silica gel was then transferred into a mortar to which hydrochloric acid of pH 1.7 was added dropwise while the mass was agitated continuously. After addition of 12.5 ml. of the stationary phase, the silica gel still remained free-flowing. It was then transferred into a flat bottomed flask with standard glass joint so as to fit the partition column. Benzene previously equilibrated with the stationary phase was used as the mobile phase, and a sufficient quantity was poured into the flask, so that the silica gel was completely covered with benzene. The contents were shaken well so as to remove the entrapped air bubbles.

A 50 cms long and 2 cms in internal diameter pyrex glass column having B.19 female joint at the top and B.7 pair of joints at the bottom was used and some quantity of the mobile phase was initially charged into it. The flask containing silica gel was now inverted on the glass column so that the standard joints fitted with each other and the silica gel was now allowed to pass into the pyrex column and settle down uniformly. Care was taken to prevent air bubbles from sticking inside the column. The prepared column was now kept under nitrogen pressure to adjust the flow rate to 2 ml/min. Finely cut and soft glass wool was packed at the top and the bottom of the silica gel packing. The effective dimensions of the partition column were kept as 13 cms long and 2 cms in diameter.

Charging of the Sample in the Column: The charging of the sample was carried out with the help of a small capsule with a ring at the top. A 50 cms long glass rod with a fine drawn hook to fix with the ring of the capsule was prepared. The sample was directly weighed in the glass capsule and was charged inside the column by the long-drawn glass rod having a hook to hold and discharge the capsule. The arrangement provided easy take-off of the capsule from the column and subsequent recharging without disturbing the column.

Chromatographic Separation: The experiments were carried out by the technique of liquid-liquid partition chromatography, and the results in this communication form only a portion of the entire data obtained and represent those most representative in character. After having charged the sample, benzene was poured on the column. 10 ml fractions were collected in glass stoppered graduated 10 ml cylinders and band spreads and peak fractions of the individual components were determined. The synthetic mixture was also eluted by benzene under identical conditions. The separated components of the mixtures were detected by comparing the band spreads and peak fractions with the individual components (Fig. 2).

Estimation of the Separated Fractions: The estimation of quinoline and iso-quinoline was carried out on a conductivity meter provided with a magic eye null-point indicator*. 25 ml of N/50 hydrochloric acid was added in each case to the varying amounts of the individual bases. The quantity of hydrochloric acid in all the cases was in excess over the bases contained in the beakers. The conductivities of the different solutions were measured (Table 1). The quantities of the bases plotted against the observed conductivities gave straight line in the region of 0 to 35.0 mg in the case of quinoline and 0 to 30.5 mg in the case of iso-quinoline (Fig. 1). The amount of bases in each of the

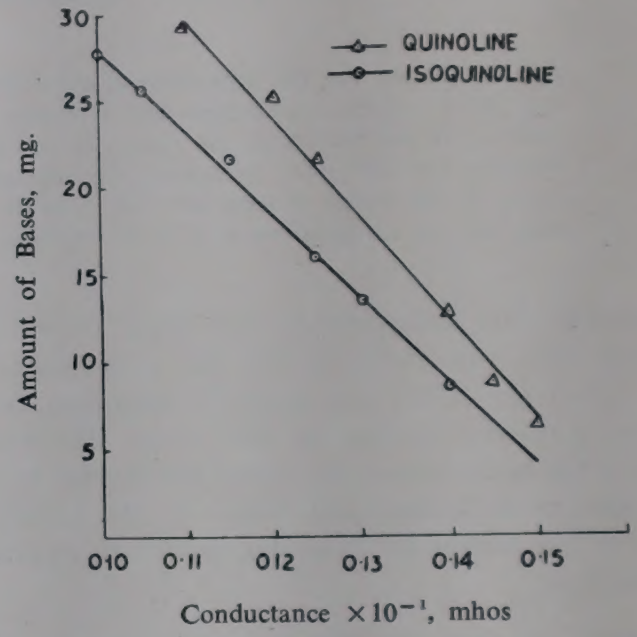

Fig. 1—Conductivity of Quinoline and Iso-quinoline.

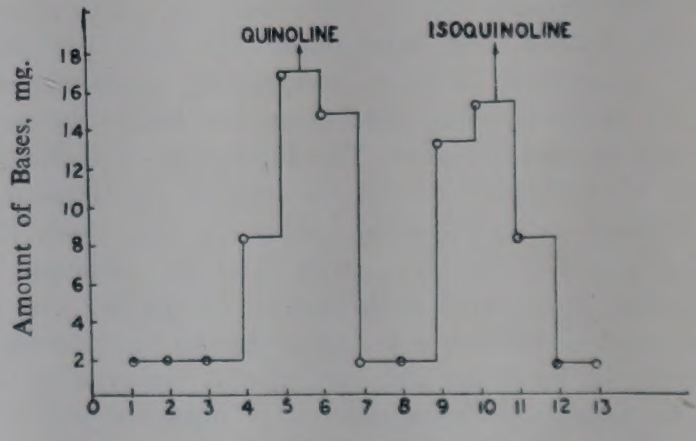

Fig. 2—Chromatographic Separation of the Mixture of Quinoline and Iso-quinoline.

* Toshninal's make—Type CL.01

TABLE 1—CONDUCTIVITY OF QUINOLINE AND ISO-QUINOLINE

Sl. No.	*Quinoline*			*Iso-quinoline*		
	Quantity mg.	*Volume of N/50 HCl, ml.*	*Observed Conductance, mhos* $\times 10^{-1}$	*Quantity mg.*	*Volume of N/50 HCl, ml.*	*Observed Conductance mhos* $\times 10^{-1}$
1	0.0	25.0	0.160	0.0	25.0	0.160
2	6.5	25.0	0.150	8.5	25.0	0.140
3	8.7	25.0	0.145	13.5	25.0	0.130
4	12.9	25.0	0.140	15.9	25.0	0.125
5	21.6	25.0	0.125	21.5	25.0	0.115
6	25.0	25.0	0.120	25.7	25.0	0.105
7	29.7	25.0	0.110	27.6	25.0	0.100

TABLE 2—CHROMATOGRAPHIC SEPARATION OF QUINOLINE AND ISO-QUINOLINE

(Q=Quinoline; IQ=Iso-quinoline)

	Q fraction, quantity charged=35.4 *mg.*		*IQ fraction, quantity charged*=28.9 *mg.*		*Mixture of Q & IQ* %*Q*=52.88 &% *IQ*=47.12	
Fraction No. (10 *ml*)	*Obs. Condn., mhos* $\times 10^{-1}$	*Qty. found from graph, mg.*	*Obs. Condn., mhos* $\times 10^{-1}$	*Qty. found from graph, mg.*	*Obs. Condn., mhos* $\times 10^{-1}$	*Qty. found from graph, mg.*
1	0.160	0.0	0.160	0.0	0.160	0.0
2	0.160	0.0	0.160	0.0	0.160	0.0
3	0.160	0.0	0.160	0.0	0.160	0.0
4	0.160	0.0	0.160	0.0	0.150	6.5
5	0.130	18.0	0.160	0.0	0.135	15.0
6	0.140	12.9	0.160	0.0	0.140	12.9
7	0.153	5.0	0.160	0.0	0.160	0.0
8	0.160	0.0	0.160	0.0	0.160	0.0
9	0.160	0.0	0.140	8.5	0.135	11.5
10	0.160	0.0	0.130	13.5	0.130	13.5
11	0.160	0.0	0.145	6.5	0.145	6.5
12	—	—	0.160	0.0	0.160	0.0
13	—	—	0.160	0.0	0.160	0.0
Total amount Eluted out:		35.9 mg		28.5 mg		%Q=52.2 %IQ=47.8

separated and eluted fractions of the partition column was calculated, by comparison with the reference standard prepared previously.

The following procedure was adopted for the estimation of the amount of bases present in each 10 ml of the eluted fraction. Each 10 ml eluted benzene fraction was extracted with 25 ml of N/50 hydrochloric acid and the acid layer now containing the bases was separated and conductances were measured. The results are given in Table 2. The measured conductances gave corresponding amounts of the bases present by a reference to the standard graph.

Recovery of Eluant: Eluted benzene fractions used in the estimation of the bases were collected together, shaken well with dilute sulphuric acid and then washed with water several times until the aqueous phase became neutral. To this treated benzene, anhydrous calcium chloride was added and kept overnight. It was then distilled and the fraction boiling between 78 to 80°C was collected. This recovered benzene solvent was

found to be pure and was used in subsequent experiments.

Discussion

The column prepared was found to be quite stable and several experiments could be carried out on it without affecting the column. It is a known fact that if the columns are stable for two to three weeks, they will remain so for a long time provided they are not disturbed[7]. The column remained pure before and after the experiment as no hydrochloric acid (stationary phase) was found depleted out of the partition column. In most of the cases, a total elution of the components was observed, which showed the efficiency of the column for almost complete base elution. In liquid-liquid chromatography, separation is effected by the distribution of the components between stationary liquid phase and mobile phase. It was observed that since iso-quinoline partitions more into hydrochloric acid and is retarded with respect to quinoline, whereas the latter partitions more in the mobile benzene phase, a separation of these two components could be achieved. A column with pure water as stationary phase was tried with benzene as eluant when the separation of the component was not effected as the bases were found to have almost the same band spread and the peak fractions. The column was therefore unsuitable for separation and was discarded. The retention time of the bases in water phase column was found to be very low as peak fractions for both the compounds were found to be in the third fraction. The column containing hydrochloric acid as the stationary phase used and described above was found to have a number of advantages such as the solvent required for complete separation and elution of the components was as low as 130 ml. The peak fractions of quinoline and iso-quinoline were found in the fifth and tenth fractions and band spreads 40 to 70 ml and 90 to 120 ml respectively, showing thereby a sharp separation of the mixture into individual components (Fig. 2). Golumbic and Orchin[8] have studied the partition co-efficient of quinoline bases by Craig's counter-current distribution technique from which it can be shown that 2-methyl quinoline and 8-methyl quinoline having close boiling points will be eluted out along with other derivatives of quinoline prior to quinoline. On the above principle, the partition column used and described earlier has been found to be efficient for the separation of quinolines from iso-quinoline. By studying the chromatographic behaviour it is observed that iso-quinoline is a stronger base than quinoline, which is in accordance with the known properties of the bases. The use of the pair of solvents mentioned earlier for the stationary and mobile phases showed no tailing of the bands which indicates the efficiency of the solvent selection. The process developed for separation of quinoline from iso-quinoline was thus found to be most efficient.

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Detection of Metal Cations in Soil by Chromatographic and Ionophoretic Techniques

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A rapid and accurate method for the separation and detection of metal cations like iron, zinc, aluminium, manganese, copper, calcium, molybdenum, magnesium and boron, present in soil, by chromatography, ionophoresis and thin layer chromatography has been worked out and the technique standardized. The coloured bands and rings corresponding to each individual metal cation were visualized by treating the chromatograms with 1 per cent w/v alizarin solution in absolute alcohol and subsequent exposure to ammonia vapour.

Inorganic substances absorbed from the soil vitally affect plant nutrition and after absorption, influence the growth from germination to full maturity and consequently the plant yield, both in quality and quantity. Although according to the present state of our knowledge practically all the elements have been shown to be present in plant material, only a few are indispensable for its growth. Some of these have been classified as essential elements, while others found in traces are called micronutrients. These include carbon, oxygen, hydrogen, nitrogen, phosphorus, potassium, calcium, sodium, chlorine, iron, zinc, aluminium, magnesium, sulphur, boron, copper, manganese, molybdenum and cobalt. While often the presence of some of these elements is still regarded unnecessary, yet the recent findings seem to justify their inclusion as essential elements and micronutrients[1].

More often, some of the metal cations are present in the soil in very small quantities and cannot be estimated by ordinary chemical methods. The application of spectrophotometric methods have now enabled, to a great extent, an accurate determination of these constituents. However, these methods are based on specialized equipments and techniques and do not find universal application. An analysis of the average range of soil constituents based on chemical as well as photometric methods has been given by Bear[2]. More recently chromatographic and ionophoretic techniques[3] have been established by which the metal cations may be separated and determined and such expeditious analytical procedure would be of particular value was emphasized by Smith[4]. Copper, cobalt, nickel, zinc, iron, manganese and molybdenum group of metals may be separated and determined by an adaptation of the procedure of Hunt and co-workers[5], which, originally meant as a geochemical prospecting technique, has since been adapted for the determination of smaller concentrations of these metals in cereals and vegetable crops[6]. Further modifications have since been made concerning chiefly the determination of zinc, molybdenum, manganese and iron by an initial concentration of the metal thereby greatly increasing the sensitivity of the technique.

Thin layer chromatography[7] and electrophoresis[8,9], both of recent origin, have proved effective tools for separation, detection and estimation of metallic ions in soil.

In this communication, an investigation on the detection and separation of metal cations in the soil by paper and thin layer chromatography and ionophoretic techniques has been made for standardizing a procedure for rapid and accurate analysis.

Experimental & Results

For comparison and standardization of analytical techniques, standard solutions of metal salts given below were prepared separately in such a way that the final metal ion concentration of the solution was as near to 0.1 per cent w/v as possible. These solutions were later acidified by the addition of a few drops of dilute hydrochloric acid. All the chemicals used were

either AnalaR B.D.H. or guaranteed reagents of E. Merck. For copper, iron, aluminium, magnesium, manganese, calcium, molybdenum, zinc and boron, the chemicals used were $CuSO_4$, $FeCl_3$, $Al(NO_3)_3$, $MgSO_4$, $MnSO_4$, $CaCl_2$, MoO_3, $Zn(NO_3)_2$ and H_3BO_3 respectively. The separation and detection of the cations were carried out by paper chromatography by descending, circular or radial flow and thin layer chromatographic techniques. A method for their detection by ionophoretic techniques (electrophoresis) was also worked out.

The results here form only a fraction of the entire data obtained and represent those most representative in character.

1. Paper Chromatography

For separating and detecting by descending and circular paper chromatographic techniques, Whatman No. 1 chromatographic paper was used. The chromatograms were developed by the dipping technique in 1 per cent w/v solution of alizarin in absolute alcohol and subsequent exposure to ammonia. The excess ammonia was removed by aeration when bands or rings corresponding to individual cation became distinctly visible, after a few minutes. Each of the cations separately and in equal volume mixtures was processed earlier, and the R_f values determined under identical conditions for comparison.

A. Descending Paper Chromatographic Technique: The solvent mixture for the descending technique consisted of ethyl-methyl ketone, amyl alcohol and conc. hydrochloric acid in the ratio 3 : 5 : 2 v/v. The chromatograms were run in a multipurpose chromatographic chamber under equilibrium conditions for 5 hours at 26°C. The bands were visualized in the manner described above. Application of this technique showed seven distinctly clear and two feeble bands corresponding to each individual metal cation. The two feeble bands corresponded to those of molybdenum and manganese. The R_f values of the cations are given in Table 1.

B. Circular or Radial Flow Paper Chromatographic Technique: Among the number of solvent systems tried for this technique, a mixture comprising n-butanol, ethyl alcohol, glacial acetic acid and water in the ratio 4 : 4 : 1 : 1 v/v for the mobile phase was found most suitable. The experiments were carried out in an all-glass circular paper chromatography tank using circles of Whatman No. 1 paper of 30 cm diameter. The chromatograms were run under identical and equilibrium conditions for 3 hours at 26°C and were developed in the manner stated earlier when the rings corresponding to these cations were observed. Application of this technique showed four distinctly clear rings for each individual metal cation and two feeble rings, the latter corresponding to the groupings of iron and zinc; and manganese and aluminium which got mixed up due to the close proximity of their R_f values. The results have been given in Table 2.

TABLE 1—R_f VALUES OF METAL CATIONS DETERMINED INDIVIDUALLY AND IN MIXTURES ALONG WITH THE COLOUR OF BANDS BY DESCENDING PAPER CHROMATOGRAPHIC TECHNIQUE

(Values in Descending Order)

			R_f Values	
S. No.	*Metal Cation*	*Colour of Band*	*Individual*	*In Mixture*
1	Iron	Bright violet	0.96	0.98
2	Zinc	Violet	0.89	0.90
3	Calcium	Yellow-orange	0.78	0.79
4	Boron	Yellow	0.69	0.70
5	Molybdenum	Reddish violet	0.60	0.58
6	Copper	Violet	0.50	0.48
7	Manganese	Reddish-violet	0.13	0.14
8	Magnesium	Violet	0.08	0.08
9	Aluminium	Reddish-violet	0.05	0.05

TABLE 2—R_f VALUES OF METAL CATIONS DETERMINED INDIVIDUALLY AND IN MIXTURES ALONG WITH THE COLOUR OF RINGS BY CIRCULAR PAPER CHROMATOGRAPAIC TECHNIQUE

(Values in Descending Order)

			R_f Values	
S. No.	*Metal Cation*	*Colour of Ring*	*Individual*	*In Mixture*
1	Boron	Deep yellow	0.78	0.80
2	Iron	Violet	0.70	0.70
3	Zinc	Violet	0.68	0.70
4	Aluminium	Reddish-violet	0.58	0.55
5	Manganese	Reddish-violet	0.52	0.55
6	Copper	Violet	0.48	0.46
7	Molybdenum	Reddish-violet	0.28	0.30
8	Magnesium	Violet	0.22	0.22
9	Calcium	could not be detected distinctly		

2. Thin Layer Chromatography

In this technique smooth and even surfaced glass plates coated by adsorbent material known as chromatoplates or chromaplates were first prepared by coating the surface of plate glass strips, 2.5 cm. wide and 30 cm. long, by a slurry mixture comprising Plaster of Paris

and chromatographic grade alumina of 200 mesh (B.S.S.) in the ratio 1 : 7 w/w with sufficient water by a thin layer spreader. The chromatoplates were dried at 30°C and the alumina over it was activated by heating at 100°C for 30 minutes immediately before use. The chromatoplates were then cooled rapidly and the solution containing the metal cation was applied 2.5 cm. above the base line, dried and placed in vertical position in an all-glass ascending chromatography tank having mobile solvent system under equilibrium conditions. The chromatoplates were run for 3 hours at 34°C and of all solvent systems the mobile one comprising n-butanol, ethyl-methyl ketone, amyl alcohol and acetic acid glacial in the ratio 10 : 10 : 5 : 2 v/v was found most suitable. The chromatoplates were later sprayed by 1 per cent w/v solution of alizarin in absolute alcohol and the individual bands corresponding to each individual metal cations were observed in the manner described above. All the bands were quite distinct; however only one band for the grouping calcium and manganese and another combined band for the grouping zinc and aluminium were obtained, since their R_f values were found very close to one another. The results are given in Table 3.

TABLE 3—R_f Values of Metal Cations Determined Individually and in Mixtures by Thin Layer Chromatography

(Values in Descending Order)

S. No.	Metal Cation	Colour of Band	R_f Values	
			Individual	In Mixture
1	Boron	Bright yellow	0.90	0.90
2	Iron	Deep violet	0.85	0.87
3	Aluminium	Reddish-violet	0.83	0.84
4	Zinc	Reddish-violet	0.81	0.84
5	Copper	Deep violet	0.78	0.80
6	Molybdenum	Reddish-violet	0.75	0.77
7	Manganese	Violet	0.65	0.70
8	Calcium	Violet	0.62	0.70
9	Magnesium	Violet	0.20	0.22

3. Electrophoresis

The experiments were carried out on a L.K.B. Producter, Swedish-make Electrophoresis Apparatus Model No. 3276 B.

Ionophoretic analysis was carried out in the polystyrene casette electrophoresis tank having platinum anode and stainless steel cathode. Carl Schleicher and Schull No. 2043 B (120 g/m²) filter paper strips 40×410 mm. were used for the electrophorograms. The buffer solution in the two electrode vessels consisted of 0.1 M Sodium Acetate: 0.1 M Acetic Acid Glacial having pH 4.5, and about 1250 ml. of this solution were required for the formation of a buffer bridge between the two electrode vessels. The power supply was kept constant at 200 V and the electrophorograms were run for 4½ hours at 30°C. The relative distances travelled by each cation between the point of charge and the electrode is denoted by R_d. These values for individual cations separately and in equal volume mixtures were determined earlier under identical conditions for comparison. The paper electrophorograms were developed by a spray of 1 per cent w/v solution of alizarin in absolute alcohol by the technique described earlier when stable bands were obtained. However, it was not considered necessary to expose the electrophorograms to ammonia until the bands corresponding to the metal cations became faint. Application of ionophoretic technique showed six well-defined and distinctly clear and one broad band corresponding to the group of metal cations viz. manganese, calcium and aluminium on the electrophorogram. The results are given in Table 4.

TABLE 4—R_d Values of Cations Determined Individually and in Mixtures along with Colour of Bands by Electrophoretic Technique

(Values in Ascending Order)

S. No.	Metal Cation	Colour of Band	R_d Values	
			Individual	In Mixture
1	Boron	Bright yellow	0.03	0.06
2	Iron	Deep violet	0.13	0.14
3	Molybdenum	Reddish violet	0.19	0.20
4	Copper	Deep violet	0.29	0.28
5	Manganese	Violet	0.34	0.35
6	Calcium	Violet	0.37	0.35
7	Aluminium	Violet	0.40	0.35
8	Magnesium	Violet	0.50	0.53
9	Zinc	Reddish violet	0.55	0.60

Discussion

The separation and detection of metal cations commonly present in soil have been carried out by descending and circular paper chromatography, thin layer chromatography and ionophoretic techniques. By the descending paper chromatography, iron, zinc, aluminium, magnesium and copper were separated distinctly, while calcium and boron were developed faintly on the chromatogram. Circular paper chromatography gave distinct rings of boron, iron, zinc and

copper, while those of aluminium and manganese were very close to each other on the paper chromatograms. Thin layer chromatography gave good separation of boron, iron, aluminium, zinc, copper and magnesium but calcium and manganese were not well separated on the chromaplates. By the ionophoretic technique, boron, iron, molybdenum, copper and zinc were very distinctly separated and detected but here again calcium and manganese separated faintly along with aluminium. It was observed that the transition elements separated very well and distinctly developed, whereas calcium and manganese were generally not clearly separated in most of the cases. The above techniques were found successful in detecting the metal cations present in as low a concentration as 0.05 mg. in most of the cases. The techniques developed provide an easy, accurate and rapid method of detection of metal cations in soil.

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The authors' thanks are due to Dr. K. R. Chakravorty, General Manager, for his interest in this work.

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Determination of Moisture by a High Frequency Titrator Part II: Moisture in Some Fertilizers

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A method based upon the use of a high frequency titrator has been developed for the determination of moisture in three fertilizers, viz. ammonium sulphate-nitrate, calcium ammonium nitrate and nitrophosphate. A suitable mixture of metnanol and dioxan is added to the samples of a fertilizer containing different quantities of moisture and a standard curve is drawn by plotting the meter reading of the salt-solvent system against moisture content in the salt. From the curve, the unknown moisture in a sample of the fertilizer can be determined.

Considerable work has been carried out by different investigators on the determination of moisture in solid materials. The techniques employed include drying the material at 100°C and above, application of Karl Fischer titration and measurements of physical properties like conductivity and dielectric constant. Some references to such types of investigations have been given in a previous communication[1]. Other recent

developments include the application of scattering and moderation of neutrous[2,3] and of nuclear magnetic resonance[4].

Many of these methods are cumbersome and time consuming, while some are not of general applicability. Thus, for example, many solid materials decompose when heated at 100°C and above and hence their moisture contents cannot be determined by this method. Some fertilizer salts and mixtures belong to such category of solids. The moisture in them has been determined by vacuum desiccation[5], vacuum oven[6], Karl Fischer[7], azeotropic distillation[8] and some other methods. Since in the previous communication[1] it has been shown that moisture in ammonium bicarbonate can readily be determined by high frequency titrimetry, it was thought desirable to study the applicability of this method to the determination of moisture in fertilizer salts. The results of these studies on three fertilizers, viz. calcium ammonium nitrate, nitrophosphate and ammonium sulphate nitrate, having ammonium nitrate as a common constituent, are reported in this paper.

Experimental

The high frequency titrator used in these investigations has already been described before[1]. The apparatus has a conductivity cell with no contact between the plates and solution, thereby removing many errors inherent in the usual conductivity cell. It contains a circuit which gives a direct indication of changes in effective overall conductance and capacitance of a titration cell, the values being read on a calibrated capacitor dial or on a valve voltmeter.

The cell used in these experiments is a thin-walled boro-silicate glass tube of 15 mm. inside diameter and 1 mm. wall thickness having a length of 65 mm. between the sleeves. The sleeves are of aluminium strips 14 mm. wide.

The experimental procedure is similar to that described earlier. The typical analysis of the important constituents in these fertilizers are given below:

Ammonium Sulphate Nitrate, %

Ammoniacal N - 19.74; Nitrate N - 6.82.

Calcium Ammonium Nitrate, %

Ammoniacal N - 10.27; Nitrate N - 10.44.

Nitrophosphate, %

Ammoniacal N - 8.10; Nitrate N - 5.70; Total P_2O_5 - 13.15; Water-soluble P_2O_5 - 5.95.

In the method employed, a weighed amount of the sample is quickly extracted with an appropriate solvent and placed in the cell of the high frequency titrator. Because of the higher solubilities of water and ammonium nitrate when a polar solvent like methanol is used, the loading effect tends to be high, thereby causing a low response to change in moisture content, although the total response is high. On the other hand, when a non-polar solvent like dioxan is used only a small portion of ammonium nitrate and moisture dissolves and the total response is low. The ideal solvent appeared to be a mixture of polar and non-polar solvents that would dissolve water well and yet dissolve the salt only enough to provide a solution with an appreciable but not excessive conductivity. This solvent is different for different fertilizers. The optimum solvent composition was determined separately by trial with different mixtures of dioxan and methanol in the case of the three fertilizers as shown in Figs. 1, 2 and 3. It will be seen that the optimum solvent compositions by volume for ammonium sulphate-nitrate, calcium ammonium nitrate and nitrophosphate are 28% methanol: 72% dioxan; 26% methanol: 74% dioxan and 24.5% methanol; 75.5% dioxan respectively.

A standard curve was drawn for each of the fertilizers using an optimum solvent system as determined above. The fertilizer sample was first dried for 2-3 hours in an oven at 50°C under a vacuum of 25 inches of mercury. Known weights of water were then added to 20 g. portions of the dry fertilizer to obtain samples of different moisture contents. The samples were ground in a mortar and pestle with small portions of the solvent and then transferred to a 100 ml wide mouth Erlenmeyer flask closed with ground glass joint and stirred for 5 min. by a magnetic stirrer. The total volume of the solvent used was 50 ml. in each case. After the stirring was completed, the mass was centrifuged for 2 min. and the supernatant liquid was transferred to the cell of the instrument which was turned on 10 min. before being used. The liquid level in the cell was kept 1 cm. above the upper metal strip and oscillation was started by adjusting the two capacitor dials. One of these dials (main dial) was locked into a suitable fixed position while the other (second dial) was rotated to give the maximum deflection in the meter. After adjusting the zero knob at a suitable fixed position and releasing the meter to its full sensitivity, the maximum deflection in the latter corresponded to the overall conductance change. Standard curves were drawn by plotting meter readings against per cent moisture in the samples. The curves for ammonium sulphate nitrate, calcium

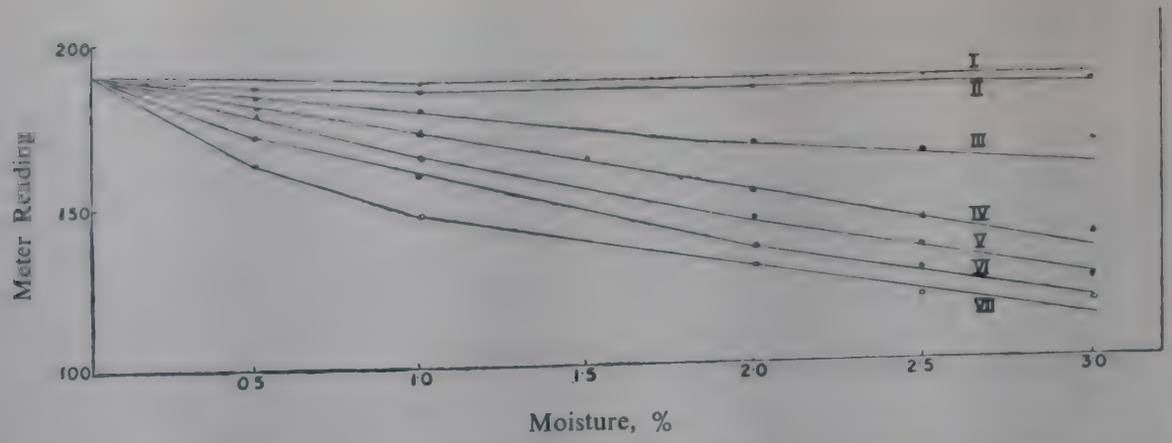

Fig. 1—Plot of Meter Reading Against Per cent Moisture in Ammonium Sulphate Nitrate with Different Proportions of Methanol and Dioxan by Volume

I—Methanol (15%)	:	Dioxan (85%)	V—Methanol (30%)	:	Dioxan (70%)
II—Methanol (20%)	:	Dioxan (80%)	VI—Methanol (40%)	:	Dioxan (60%)
III—Methanol (25%)	:	Dioxan (75%)			
IV—Methanol (28%)	:	Dioxan (72%)	VII—Methanol (60%)	:	Dioxan (40%)

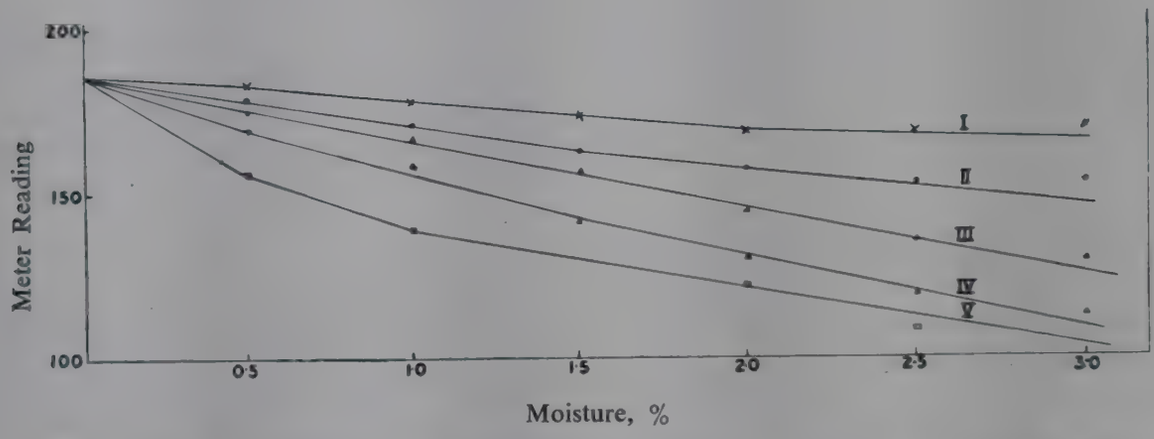

Fig. 2—Plot of Meter Reading against Per cent Moisture in Calcium Ammonium Nitrate with Different Proportions of Methanol and Dioxan by Volume

I—Methanol (20%)	:	Dioxan (80%)	IV—Methanol (30%)	:	Dioxan (70%)
II—Methanol (23%)	:	Dioxan (77%)			
III—Methanol (26%)	:	Dioxan (74%)	V—Methanol (40%)	:	Dioxan (60%)

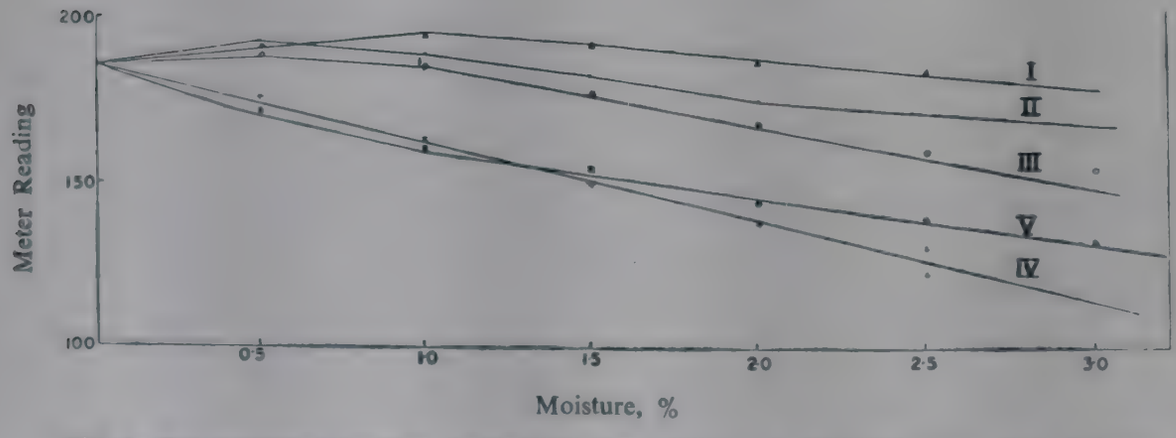

Fig. 3—Plot of Meter Reading Against Per cent Moisture in Nitrophosphate with Different Proportions of Methanol and Dioxan by Volume

I—Methanol (40%)	:	Dioxan (60%)	IV—Methanol (24.5%)	:	Dioxan (75.5%)
II—Methanol (60%)	:	Dioxan (40%)			
III—Methanol (30%)	:	Dioxan (70%)	V—Methanol (20%)	:	Dioxan (80%)

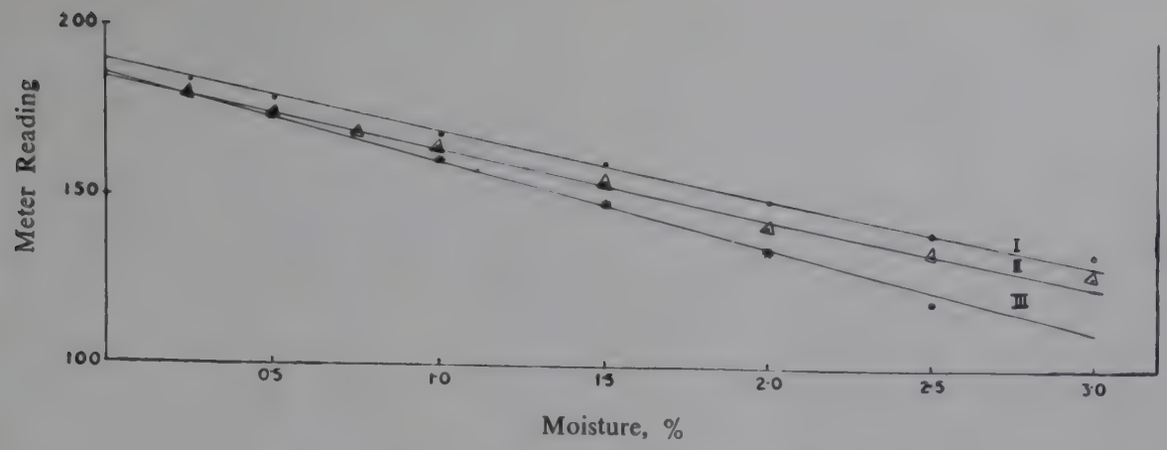

Fig. 4—Moisture in Different Fertilizers: Standard Curves

I—Ammonium Sulphate Nitrate. Solvent used: Methanol 28 per cent, Dioxan 72 per cent
II—Calcium Ammonium Nitrate. Solvent used: Methanol 26 per cent, Dioxan 74 per cent
III—Nitrophosphate. Solvent used: Methanol 24.5, Dioxan 75.5 per cent

ammonium nitrate and nitrophosphate are shown in Fig. 4.

Results and Discussion

Moisture in different lots of the three fertilizers was determined from the standard curves and the values were compared with those obtained by the vacuum oven method in which the losses in weight of the samples were determined by drying the samples for 2-3 hours at 50°C under a vacuum of 25 inches. There was close agreement between the two sets of values (Tables 1-3). The high frequency titrator method gives accurate results up to a moisture content of 3 per cent.

TABLE 1—Moisture Determination in Ammonium Sulphate-Nitrate

Sample No.	*Moisture Determined by Vacuum Oven Method, %*	*Moisture Determined by High Frequency Titrator Method*	
		Meter Reading	*Moisture, %*
I (Uncoated)	1.56	160	1.52
II „	0.50	180	0.49
III „	2.18	147	2.19
IV „	0.32	183	0.32
V „	1.14	167	1.15
VI (Coated)	1.97	151	2.00
VII „	2.04	149	2.08
VIII „	2.41	143	2.39
IX „	0.78	175	0.75

The high frequency titrimetry thus provides a convenient method of estimating moisture in fertilizer salts. Once the standard curve is drawn for a fertilizer, the moisture in it can be estimated within fifteen minutes.

TABLE 2—Moisture Determination in Calcium Ammonium Nitrate

Sample No.	*Moisture Determined by Vacuum Oven Method, %*	*Moisture Determined by High Frequency Titrator Method*	
		Meter Reading	*Moisture, %*
I	2.68	131	2.67
II	1.72	150	1.71
III	2.13	142	2.11
IV	1.11	163	1.10
V	0.84	168	0.83
VI	0.44	175	0.44
VII	0.22	180	0.21
VIII	1.98	145	1.97

TABLE 3—Moisture Determination in Nitrophosphate

Sample No.	*Moisture by Vacuum Oven Method, %*	*Moisture Determined by High Frequency Titrator Method*	
		Meter Reading	*Moisture, %*
I	1.82	141	1.82
II	0.76	167	0.76
III	2.14	133	2.12
IV	1.21	155	1.22
V	0.18	181	0.17
VI	2.24	130	2.22
VII	1.45	150	1.44

The method is therefore suitable for plant control operations.

Acknowledgement

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Cation Exchange Resin from Waste Acid Sludge Part I—Description and Properties

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Cation-exchange resins have been prepared from waste acid suldge of by-product coke oven industry. This resin is highly stable, and is found suitable for treatment of water and purification of aqueous solutions, even under conditions of high pH and temperature. Its various properties, like exchange capacity, stability, particle size, etc., have been discussed.

In the benzol refining process of by-product coke oven industry, a large amount of acid sludge is produced as a waste product. In such a plant, having capacity of carbonization of about 4,000 tons/day of coal and producing 8,000 gallons of crude benzol approximately, the acid sludge production is of the order 2 tons/day[1].

Formation and Nature of Acid Sludge: During the refining of crude benzol by concentrated sulphuric acid washing, a large number of organic compounds present polymerize resulting in the formation of gummy and resinous substances, which are slightly soluble in oil and form a black, highly viscous, tar-like corrosive sludge, having an obnoxious odour. The acid sludge or acid tar, as it is called, contains a large quantity of unused sulphuric acid and entrained oil. In some plants the acid wash is done in two stages producing acid sludges of different acidity. The nature and composition of the sludge is shown in Table 1.

TABLE 1—Composition of Acid Sludge

Specific gravity	..	..	1.20-1.30
Sulphuric acid, % w/w	..	..	20-50
Benzol content „	..	..	20-35
Solid content „	..	..	30-60
Nitrogenous base „	..	..	0.4-0.6

Disposal of Acid Sludge: The disposal of the acid sludge is a difficult problem due to its highly corrosive nature and obnoxious smell. In the past, many attempts have been made for treating it in various ways such as recovery of sulphuric acid and other hydrocarbons from it, etc., but none of these proved economical. In major cases it is taken to a spot away from habitation and surface or ground water sources and dumped in a pit. In some cases, it is also disposed of by burning in a suitably designed equipment.

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A thorough investigation on the nature and characteristics of the acid sludge obtained from the acid washing of crude benzol of a coke oven plant resulted in the development of a process for the preparation of an ion-exchange resin of immense industrial value. Various types of ion-exchange resins have been prepared from the acid sludge, suitable for different specific uses. Most of ion-exchange resins are used mainly for water treatment under varying operating conditions, like pH, temperature and characteristics of water to be treated.

Preparation of Cation Exchange Resin: The cation-exchange resins are prepared from the acid sludge obtained from the acid washing of crude benzol of by-product coke oven plant. The processes of preparation are patented by FCI Ltd[2,3].

Results & Discussion

Characteristics of Resin: The above resin is a hard, granular, porous material which swells to some extent when immersed in water and is capable of exchanging cations from solution. The characteristic exchange groups in the resin have been determined according to Gregor et al[4], by the typical titration curve studies, wherein it is seen clearly that the two major exchange groups present are sulphonic and carboxylic (Fig. 1).

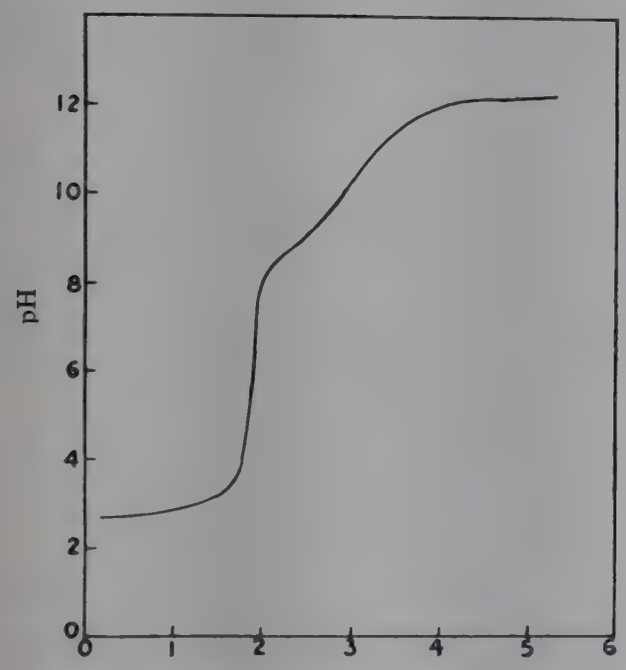

Fig. 1—Titration Curve for Cation Exchange Resin

At lower pH, mostly the sulphonic acid groups take part in the exchange, whereas at higher pH the carboxylic group also becomes effective in the exchange along with sulphonic group.

The exchange capacities, viz. strong acid or salt splitting and weak acid capacities, were determined following the method of Kunin[5] and are indicated in Table 2.

TABLE 2—Exchange Capacities of the Cation-Exchange Resin

Exchange Resin	*Strong Acid Capacity*	*Weak Acid Capacity*	*Total Capacity*
I	0.7-0.85 meq/ml	0.3-0.75 meq/ml	1.0-1.6 meq/ml
	1.5-2.0 meq/g.	1.5-3.0 meq/g.	3.0-5.0 meq/g.
II	0.5-0.80 meq/ml	0.7-1.0 meq/ml	1.2-1.8 meq/ml
	1.1-1.9 meq/g.	1.4-2.1 meq/g.	2.5-4.0 meq/g.

The swelling property, colour throw and attrition characteristics, which are the different measures of stability of resin, have been studied at different pH and temperature (Tables 3 and 4). The resin has been found highly stable under conditions of use in water treatment. The high swelling resins are normally less suitable at high temperature and pH conditions. With organic solvents like benzene, toluene, etc., it has been found to be very stable as it does not throw any colour. The revolving circular disc method[6] was adopted here for finding out the attrition characteristics (Table 4).

TABLE 3—Swelling and Stability of Cation-Exchange Resin

(The colour throw measured by light transmission at 530 mμ while comparing with distilled water as standard)

Exchange Resin	*Swelling (H^+ Form, in Contact with Water, %*	*Stability*		
		Colour Throw at 30°C upto pH 13	*Colour Throw at 60°C upto pH 12*	*Colour Throw at 90°C upto pH 11*
I	60-70	nil (very stable)	very slight (stable)	very slight (stable)
II	20-30	nil (very stable)	nil (very stable)	nil (very stable)

TABLE 4—Attrition Values of the Exchanger

[Test performed at 30°C with 16 to 52 mesh (B.S.S.) fraction]

Exchange Resin	*Turbidity, ppm*	*Attrition Number*	*Remarks*
I	15-20	500-700	very stable
II	9-12	850-1100	very stable

Application

The application of this resin in water treatment has been studied in columns set up in the laboratory and pilot plant and also in commercial plants at F.C.I. Sindri. The resin size, void volume in column, backwash characteristics, pressure drop across the bed are given in Table 5.

TABLE 5—OPERATING CHARACTERISTICS OF THE CATION-EXCHANGE RESIN

Particle size, mm.	0.30-12.0
Effective size, mm.	0.4 -0.5
Uniformity coefficient	1.8 -2.3
Void volume in column, %	38-42
Backwash characteristics	Backwash flow rate 4.5 gals/sq.ft./min for 50% bed expansion at the temp. 30°C
Pressure drop	0.2 lbs/sq. inch/ft. of bed height for the flow rate of 5.0 gals/sq.ft/min. at the temperature 30°C

TABLE 6—OPERATING CAPACITIES OF THE CATION-EXCHANGE RESIN UNDER VARIOUS CONDITIONS OF REGENERATION AND EXHAUSTION

	Regenerant	*Exhaustant*	*Operating Capacity, Kgr./cu.ft.*
Partial demineralisation with removal of cations	Sulphuric Acid/ Hydrochloric acid.	Sodium chloride solution in water	9-12
,,	,,	Sodium bicarbonate solution in water	12-18
,,	,,	Calcium chloride solution in water	10-18
,,	,,	River water	12-18
Base exchange with hardness removal	Sodium chloride	,,	9-14
,,	,,	Calcium chloride solution in water	9-14

In the industrial water treatment the resin used is in hydrogen form by regenerating with acid for a partial demineralization process or in the sodium form by regenerating with a sodium chloride solution for the base-exchange process. The exchange characteristics have been studied under various conditions of use. The exchange characteristics of the cation exchange resin in hydrogen and sodium forms have been investigated for various synthetic and natural waters containing sodium, calcium, magnesium ions in their chloride, sulphate, and bicarbonate forms. The operating capacities are shown in Table 6.

The cation-exchange resin in view of its high stability under alkaline conditions and high temperature was found extremely suitable for treatment of all kinds of water for industrial purposes including treatment of boiler feed water by the hot lime base-exchange process. Other applications of this cation-exchanger are in the treatment of effluents, recovery of costly metals from waste water, purification of aqueous solution, etc. Investigations are being continued for its use in various fields of application of industrial importance.

Acknowledgements

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Exchange Adsorption of Ions from Aqueous Solution by Cation Exchange Resin Prepared from Acid Sludge

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The application of different adsorption equations to the ion exchange process indicated that the Langmuir's equation is applicable in both the cases, viz. (i) where the amount of exchanger and the volume of solutions containing exchangeable ions are fixed, only the concentrations are varied, and (ii) where the amount of the exchanger is fixed but the volumes and concentrations of solutions containing exchangeable ions are varied.

The value of the constant k in Langmuir's equation has been found nearly equal to the true total exchange capacity of the ion-exchange resin studied viz. the cation exchanger produced at Sindri.

Very few physico-chemical phenomena can be applied for determining the relation between the extent of exchange and concentration of the exchanging ions in solution at equilibrium. The various attempts for solving the relationship fall into two categories—one assuming a simple adsorption process and the other applying the law of mass action. In this study only the former assumption has been taken into consideration.

Wiegner[1, 2] at first applied the Freundlich isotherm equation to ion exchange by using the relationship

$$\frac{x}{m}=kp^{1/n} \qquad .. \qquad (1)$$

where x/m is the amount of cations, expressed in milliequivalents, taken up from a solution at equilibrium with a given weight of resin expressed in grams, p, the amount of added cations remaining in the solution expressed as g.moles/l. and k and n are constants.

Later on, realising that Freundlich isotherm did not indicate a finite capacity, Wiegner and Jenny[3] modified the above relationship as

$$\frac{x}{m}=k\left(\frac{c}{a-c}\right)^{1/p} \qquad .. \qquad (2)$$

where x/m is the amount of cations in milliequivalents adsorbed per 100 g.of resin, c is the concentration of original cations remaining at equilibrium in g. moles/l. a is the initial concentration in g.moles/l. and k and p are constants.

Boyd, Schubert and Adamson[4] used the Langmuir's equation for expressing the exchange adsorption of solution ions by an ion exchange resin. The equation for one of the ions A^+ from an electrolyte solution can be expressed as

$$\left(\frac{x}{m}\right)_{A^+}=\frac{k\,b_1\,C_{A^+}}{1+b_1\,C_{A^+}+b_2C_{B^+}} \qquad .. \qquad (3)$$

where $(x/m)_{A^+}$ is the amount of ions A^+ adsorbed per unit weight of adsorbent in meq.g., C_{A^+} and C_{B^+} are the respective equilibrium concentration of ions A^+ and B^+ in solution in g.moles/l. and k, b_1 and b_2 are constants. The constant k is identified as the exchange capacity and b_1 and b_2 are related to energy of adsorption of ions.

The quantity unity in the denominator in equation (3) can be neglected relative to $(b_1\,C_{A^+}+b_2\,C_{B^+})$ to a good approximation. Therefore, the equation (3) can be written as

$$\left(\frac{x}{m}\right)_{A^+}=\frac{k\,b_1\,C_{A^+}}{b_1C_{A^+}+b_2\,C_{B^+}} \qquad .. \qquad (4)$$

The equation (4) can further be written in the form

$$\frac{C_{A^+}}{C_{B^+}} \Big/ \left(\frac{x}{m}\right)_{A^+} = \frac{1}{k}\frac{b_2}{b_1} + \frac{1}{k}\frac{C_{A^+}}{C_{B^+}} \quad .. \quad (5)$$

If this treatment is valid, the plot of $\left[\frac{C_{A^+}}{C_{B^+}} \Big/ \left(\frac{x}{m}\right)_{A^+}\right]$ and C_{A^+}/C_{B^+} should give a straight line. If very small concentration of A^+ is present in solution relative to concentration B^+, even the complete adsorption of A^+ will not desorb sufficient quantity of B^+ to cause a detectable change in C_{B^+}; as a result, a plot of $C_{A^+}/(x/m)_{A^+}$ against C_{A^+} would be expected to be linear. It has been further revealed from equation (4) that the amount of base exchange $(x/m)_{A^+}$ must depend upon the ratio of equilibrium concentration of exchanging ions.

The exchange equilibrium of the cation-exchange resin[5, 6] produced by F.C.I. Sindri has been studied for finding the relations governing the equilibrium behaviour of the adsorption system.

Experimental

The exchange resin sample has been converted to hydrogen form by passing a large excess of NHCl through the resinbed. The resin is then washed with distilled water in order to make it free from any acid adsorbed on the resin surface.

A definite fixed amount of air-dried sample (H^+ form) has been taken in nine different bottles and the equal volumes of solution of sodium chloride of different concentrations have been added to each in the order as given in Table 1.

TABLE 1

Bottle No.	*Volume of solution, cc.*	*Concentration of NaCl*
I	200	N/10
II	200	N/20
III	200	N/40
IV	200	N/80
V	200	N/100
VI	200	N/200
VII	200	N/400
VIII	200	N/800
IX	200	Nil

In the last bottle the distilled water has been added to resin sample in order to determine the acid adsorbed on the surface of resin. The moisture of the air-dried sample has been determined earlier for ascertaining the dry weight of resin.

The solutions have been kept in contact with the resin for two days with intermittent shaking to attain equilibrium at a constant temperature of 37°C. The concentrations of the supernatant solution have been estimated in each bottle (Table 3).

In another set of nine bottles, a fixed amount of air-dried resin sample (H^+ form) has been taken and different volumes of solution of sodium chloride of different concentration have been added to each one in the manner given in Table 2. The results, obtained in the same manner as in the first case, are given in Table 4.

With the results in Tables 3 and 4 different adsorption equations are tested.

TABLE 2

Bottle No.	*Volume of solution, cc.*	*Concentration of NaCl*
I	190	N/9.5
II	175	N/17.5
III	150	N/30
IV	125	N/50
V	100	N/50
VI	75	N/75
VII	50	N/100
VIII	25	N/100
IX	200	Nil

TABLE 3—VARIATION OF THE AMOUNT OF THE EXCHANGING IONS IN RESIN AT DIFFERENT CONCENTRATION OF SOLUTION AT EQUILIBRIUM
(1st Case)

(*Strong acid capacity of the exchange resin* 1.727 *meq.g.*; *Weight of dry resin taken* 1.019 *g.*; *Total exchangeable ions in the resin* 1.76 *meq.*)

Bottle No.	$C_{H_s^+}$ *g. mols./l.*	$C_{Na_s^+}$ *g. mols./l.*	$C_{Na_R^+}$ *meq.*	$C_{H_R^+}$ *meq.*
I	0.2986	5.3710	1.622	0.138
II	0.2708	2.4910	1.484	0.276
III	0.2305	1.0920	1.268	0.492
IV	0.1803	0.4423	0.988	0.772
V	0.1595	0.3312	0.868	0.892
VI	0.1113	0.1141	0.610	1.150
VII	0.0653	0.0415	0.358	1.402
VIII	0.0387	0.0111	0.212	1.548

TABLE 4—VARIATION OF THE AMOUNT OF THE EXCHANGING IONS IN RESIN AT DIFFERENT CONCENTRATIONS OF SOLUTION AT EQUILIBRIUM
(2nd Case)

(Strong acid capacity of the exchange resin 1.727 meq./g.; Weight of dry resin taken 1.015 g.; Total exchangeable ions in the resin 1.751 meq.)

Bottle No.	$C_{H_S^+}$ *g. mols./l.*	$C_{Na_S^+}$ *g. mols./l.*	$C_{Na_R^+}$ *meq.*	$C_{H_R^+}$ *meq.*
I	0.3121	5.3500	1.7100	0.0410
II	0.3193	2.8310	1.5310	0.2200
III	0.3120	1.4510	1.2830	0.4680
IV	0.2957	0.6961	1.0130	0.7380
V	0.3358	0.6318	0.9200	0.8310
VI	0.3048	0.2926	0.6263	1.1247
VII	0.2938	0.1141	0.4025	1.3485
VIII	0.3450	0.0322	0.2362	1.5148

Results and Discussion

The amounts of exchange of the resin at various equilibrium concentrations of sodium chloride solution are shown in Fig. 1. The curves 1a and 1b are of similar nature, although the latter is slightly deviated from the former.

For testing the modified form of Freundlich's equation, viz (1), a plot of log (x/m) against log p has been made for both the sets of experiments (Fig. 2). But the resultant curves are not linear throughout as expected, so the equation (1) is not strictly applicable in either of these series. This is because the exchange capacity of the cation-exchange resin is a finite quantity.

In order to test the validity of Wiegner and Jenny's equation, viz. (2), log (x/m) is plotted against log (c/a-c) for both the sets of data and the plots have been given in Fig. 3. A straight line is supposed to result but as it is not observed here so this equation also cannot be applicable to our exchange process over the whole range of concentrations. It may therefore be concluded that there is no linearity between the cations adsorbed x/m by the resin and the ratio of cations remaining in solution to those exchanged at equilibrium $\frac{c}{a-c}$.

For applying Langmuir's equation to both the sets of experiments the data have been tabulated (Tables 5 & 6). In the first case, where the constant volume of solutions of different concentrations have been taken with the fixed weight of exchanger, the plot of C_{Na^+}/C_{H^+} against $C_{Na^+}/C_{H^+}/(x/m)_{Na^+}$ has resulted to a linear one (Fig. 4a). The slope of this plot must be equal to 1/k according to equation (5).

$$\text{Slope} = \frac{1}{k} = 0.56$$

$$\therefore k = 1.78$$

Here the value of k is nearly coinciding with the true total exchange capacity (viz. 1·727), but it may not

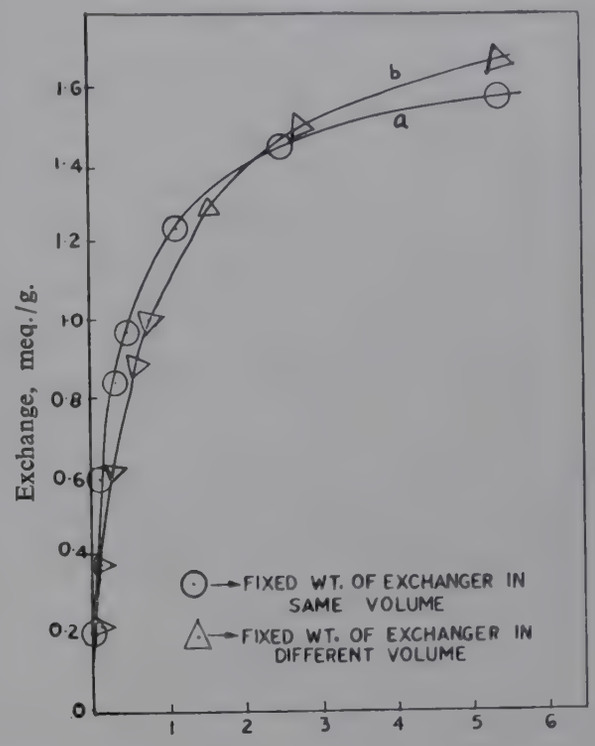

Fig. 1—Variation of Exchange for Sindri Cation Exchanger (H-Form) at Different Equilibrium Concentrations of NaCl Solution

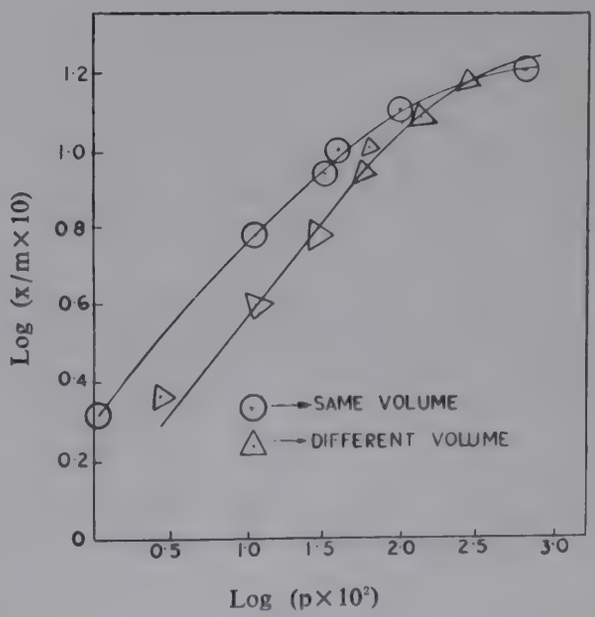

Fig.2—The Plot of Log (x/m) Against Log p in Accordance with Freundlich's Equation

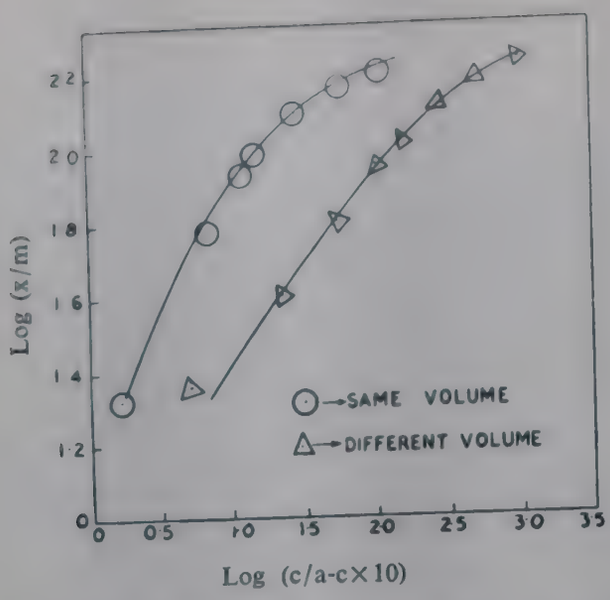

Fig. 3—The Plot of Log (x/m) Against Log (c/a-c) in Accordance with Weigener & Jenny's Equation

TABLE 5—VARIATION OF THE EXTENT OF EXCHANGE AT DIFFERENT RATIOS OF CONCENTRATIONS OF EXCHANGING IONS IN SOLUTION

(1st Case)

Bottle No.	$C_{Na_s^+}$ *g. mols./l.*	$C_{H_s^+}$ *g. mols./l.*	$(x/m)_{Na^+}$ *meq./g.*	C_{Na^+}/C_{H^+}	$\frac{C_{Na}/C_{H^+}}{(x/m)_{Na^+}}$
I	5.3710	0.2986	1.5920	17.9800	11.300
II	2.4910	0.2708	1.4540	9.1980	6.326
III	1.0920	0.2305	1.2430	4.7380	3.805
IV	0.4423	0.1803	0.9698	2.4530	2.530
V	0.3312	0.1585	0.8520	2.0900	2.452
VI	0.1141	0.1113	0.5987	1.0250	1.712
VII	0.0415	0.0653	0.3514	0.6357	1.810
VIII	0.0112	0.0387	0.2081	0.2873	1.381

TABLE 6—VARIATION OF THE EXTENT OF EXCHANGE AT DIFFERENT RATIOS OF THE CONCENTRATIONS OF EXCHANGING IONS IN SOLUTION

(2nd Case)

Bottle No.	$C_{Na_s^+}$ *g. mols./l.*	$C_{H_s^+}$ *g. mols./l.*	$(x/m)_{Na^+}$ *meq./g.*	C_{Na^+}/C_{H^+}	$\frac{C_{Na^+}/C_{H^+}}{(x/m)_{Na^+}}$
I	5.3500	0.3121	1.6850	17.1400	10.1700
II	2.8310	0.3193	1.5090	8.8680	5.8770
III	1.4510	0.3121	1.2610	4.6470	3.6760
IV	0.6961	0.2957	0.9982	2.3550	2.3580
V	0.6318	0.3358	0.9066	1.8810	2.0750
VI	0.2926	0.3048	0.6172	0.9600	1.5560
VII	0.1141	0.2938	0.3965	0.3883	0.9793
VIII	0.0322	0.3450	0.2328	0.0933	0.4006

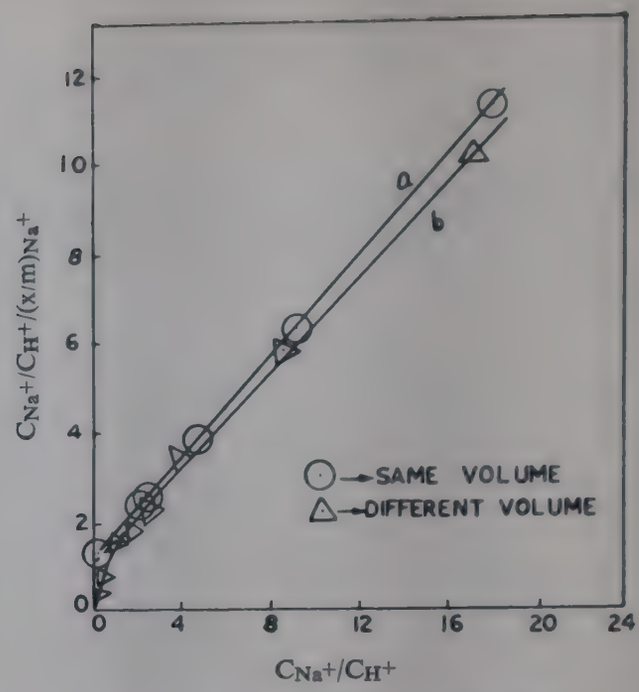

Fig. 4—The Plot of C_{Na^+}/C_{H^+} Against $C_{Na^+}/C_{H^+}/(x/m)_{Na^+}$ for testing Langmuir's Equation

be the case with every exchange process as stated by Boyd et.al.[4] As the extent of exchange at the flat portion of isotherm is represented by 'k' so it may coincide with the true total exchange capacity only in special cases.

If no adsorption had been here in the exchange process, at $C_{Na^+}=0$ the factor $[C_{Na^+}/C_{H^+}/(x/m)_{Na^+}]$ also would have been zero; so it would have resulted the intercept also to a zero value. As it is not the case observed, so it is evident that, besides exchange, adsorption is also taking place simultaneously. This adsorption is mostly of sodium ions which is in large excess compared to hydrogen ions. The value of intercept of the straight line (a) in Fig. 4 has been found as equal to 1.2, which corresponds to b_2/b_1k in equation (5).

Further, from this plot it is possible to determine the amount of exchange at any desired concentration of the exchanging ions in solution.

When the Langmuir's equation (5) is applied to the second case, where the different volumes of solutions of different concentrations are treated with a fixed amount of exchanger, a plot of C_{Na^+}/C_{H^+} against $C_{Na^+}/C_{H^+}/(x/m)_{Na^+}$ from the data given in Table 6 is obtained (Fig. 4b). It can easily be seen from the plot that it is a straight line except at a portion where it is a curve at very low concentration of sodium ions, and the curve apparently tends to terminate at the origin. This apparent deviation at lower volumes of solution at lower concentration is due to the large excess of hydrogen ions compared to sodium ions resulting in

adsorption of more of hydrogen ions than sodium ions, thereby affecting the estimation of the ions in the solution. From the slope of the straight line portion the value of k is found to be equal to 1.80 which is almost the same as in the earlier case. The extrapolated intercept i.e. b_2/b_1k was found to be 1.05.

Summary and Conclusions

(i) The various adsorption equations were applied for the exchange process taking place with the cation-exchanger being produced at Sindri.

(ii) The equation of Freundlich and its modified form by Wiegner and Jenny were observed not to be strictly applicable in this case.

(iii) The Langmuir's equation was found applicable to both the cases studied viz. (1) where the fixed amount of ion exchange resin has been treated with the fixed total volume of solution of different concentration and (2) where a fixed amount of exchanger has been treated with different volumes of solutions of different concentration.

(iv) In both the cases where Langmuir's equation is applicable, the value of constant k in the equation has been found nearly equal to the true total exchange capacity.

Acknowledgement

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Hydrodesulphurization of Petroleum Feedstock Part I—Kinetic Study on Hydrotreatment of Heptane Solution of Carbon Disulphide

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Vapour phase hydrodesulphurization of petroleum hydrocarbons has been studied using heptane with varying amounts of carbon disulphide over cobalt molybdate catalyst under atmospheric pressure. The effects of temperature and heptane and hydrogen feed rates have also been studied, and a satisfactory kinetic expression has been deduced which is verified by experimental data. Allowable space velocities for 99 per cent conversion of carbon disulphide into hydrogen sulphide have been predicted.

The rapid growth of industries based on petroleum feedstocks has necessitated the availability of relatively sulphur-free products for further processing. The catalytic hydrodesulphurization process for removal of sulphur compounds from petroleum feedstocks is an essential step for catalytic steam-reforming for production of town gas, synthesis gas, etc. Such feedstocks are always associated with different types of organic sulphur

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compounds like carbon disulphide, carbon oxysulphide, mercaptans, thiophenes[1], etc. in varying quantities. The sulphur tolerance of nickel catalyst used for catalytic steam-reforming of petroleum feedstocks for the production of synthesis gas for fertilizer manufacture has been stated to be about 5-8 ppm[2]. The rate of organic sulphur removal by hydrotreatment depends on the nature and molecular weights of organic sulphur compounds as well as on the process conditions. Earlier studies[3-9] on hydrodesulphurization were mostly limited to catalyst and process development with very few devoted to kinetic studies. The study of the fundamental kinetic characteristics of hydrotreatment of petroleum feedstocks was therefore taken up under laboratory condition.

This paper deals with the kinetic study on hydrotreatment of heptane solution of pure carbon disulphide. In subsequent papers, studies on hydrotreatment of heptane solutions of thiophene and ethylmercaptan will be dealt with. Heptane of molecular wt 100 and carbon/hydrogen ratio 5.25 has been chosen as the feedstock, since it resembles light petroleum naphtha in physicochemical properties relevant for hydrotreatment.

Theory

Wilson, Voreck and Malo[10] showed that the rate of hydrogenation in presence of cobalt molybdate catalyst of dibenzothiophene in naphtha solution is a function of the concentration of dibenzothiophene, partial pressure of hydrogen and process temperature.

Based on this information, the velocity of hydrogenation, V_H, may be expressed as

$$V_H = k_H e^{-E/RT}\, p_S\, p_H^m = k_H e^{-E/RT}\, (x_S P)\, (x_H P)^m \quad .. \quad (1)$$

$$\text{Also } V_H = -F \frac{dx_S}{dw_R} \quad .. \quad (2)$$

Hence from equations (1) & (2)

$$-F \frac{dx_S}{x_S} = k_H e^{-E/RT}\, P^{1+m}\, x_H^m\, dw_R \quad .. \quad (3)$$

Integrating

$$-\frac{F}{W_R} \ln \frac{x_{S,2}}{x_{S,1}} = k_H e^{-E/RT}\, x_H^m\, P^{1+m} \quad .. \quad (4)$$

The equation (4) shows that the rate of hydrogenation is proportional to total pressure to the power 1+m, but from the kinetic equation given by Tadao Shiba and Takeo Nagata[11] it is found that hydrogenation rate is proportional to the first power of total pressure. Hence equation (4) will represent the true effect of pressure only, when the right hand side is multiplied by $1/P^m$. After this is done equation (4) becomes

$$-\frac{F}{W_R} \ln \frac{x_{S,2}}{x_{S,1}} = k_H e^{-E/RT}\, x_H^m P \quad .. \quad (5)$$

Experimental

Apparatus: The experimental set-up comprises the following (Fig. 1): (a) an electrically-heated stainless

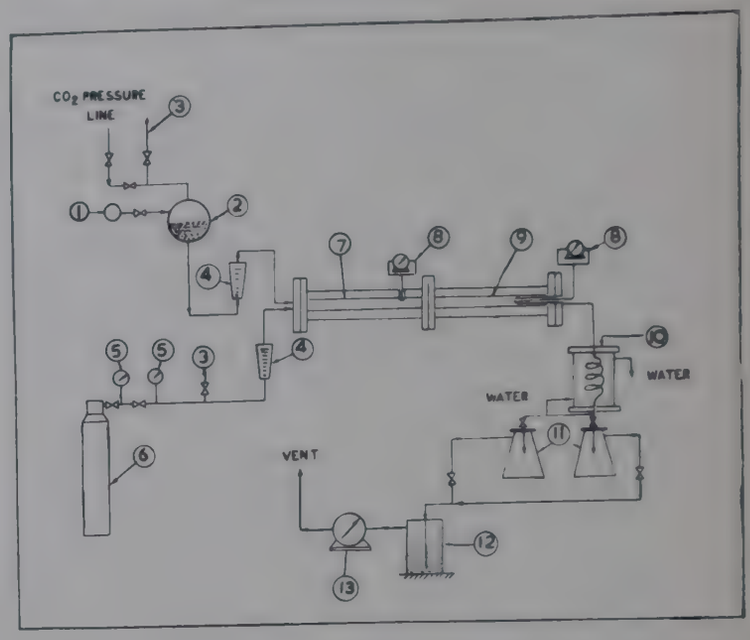

Fig. 1—Flow Diagram of Hydrodesulphurization Unit

1. Storage for heptane solution of CS_2
2. Heptane feed vessel
3. Bypass regulator
4. Rotameter
5. Pressure gauge
6. Hydrogen cylinder
7. Preheater (electrically heated)
8. Millivolt meter
9. Reactor (electrically heated)
10. Condenser
11. Condensate reciever
12. Absorption vessel, cadmium acetate solution absorbent
13. Wet gas meter

steel (type 321) pre-heater-cum-vaporizer tube, 25 mm. i.d., 600 mm. long with a thermocouple well at the outlet end; (b) an electrically heated stainless steel (type 321) reactor tube 25 mm. i.d. 600 mm. long with a thermocouple well at the outlet; (c) one water-cooled copper coil condenser; (d) two condensate receivers made of glass; (e) one wet gasometer to meter the non-condensable gas; (f) one rotameter for measuring the liquid heptane flow; and (g) one rotameter for measuring the hydrogen flow.

Before setting up the apparatus. the preheater and the reactor tubes were packed with 6 mm. alundum balls, and in-between the alundum balls and the outlet

of the reactor was placed a layer of cobalt-molybdate catalyst of known weight and size. The preheater and reactor tubes were insulated with fireclay cement and asbestos.

Materials Used: (1) Heptane—commercially pure, sp.gr. 0.718, boiling range 93-94°C; olefins 5.5 per cent, aromatic 6.5 per cent, sulphur nil (2) Carbon disulphide, chemically pure, sp.gr. 1.265 (3) Cobalt molybdate catalyst pellets—Prepared in our laboratory; Size—6 mm. dia×9 mm. long; composition (%): CoO-2.5, MoO_3-5.0, NiO-0.25, and Al_2O_3-rest (4) Hydrogen—Pure, obtained from hydrogen cylinder.

Procedure: After assembling the apparatus, the preheater and reactor were electrically heated under hydrogen atmosphere. The preheater was heated to about 150-200°C and the temperature of the reactor was maintained at the desired condition. The heptane solution of carbon disulphide was then introduced with the simultaneous adjustment of the condenser cooling water to get the condensate separated at room temperature. The heptane and hydrogen flow rates were then controlled at the desired values. The reaction temperature was controlled by varying current input to the heater windings. The non-condensable gases were then metered by a wet gasometer after passing through a cadmium acetate solution. About 40 hours were allowed for catalyst activity to reach an equilibrium value before any experimental data were collected. For any particular process condition, successive samples of gas and condensate were analysed for sulphur content until steady state (constant per cent conversion) was reached. Experimental data were taken under steady conditions with different flow rates of hydrogen and heptane at various temperatures.

Estimation of Sulphur: Quantitative estimation of carbon disulphide in heptane was done in a micro-organic sulphur estimation apparatus, standardized in our laboratory. In this apparatus, organic sulphur is first catalytically hydrogenated into hydrogen sulphide over red-hot platinum coil. Hydrogen sulphide is then absorbed in a zinc acetate solution and estimated colorimetrically by methylene blue method.

Hydrogen sulphide content of non-condensable gases was estimated by absorbing in cadmium acetate solution followed by iodometric titration.

Results

Experimental data show the percentage conversion of carbon disulphide to hydrogen sulphide at different flow rates and temperatures (Table 1). 50 g. of cobalt

TABLE 1—Experimental Data

Expt. No.	*W_R, g. of Catalyst used*	*F_H, g. moles hydrogen/hr. in feed*	*F_{HC} g. moles heptane/hr. in feed*	*F, Total feed, g. moles/hr.*	*Temp., °C.*	*CS_2 in heptane feed Wt/Wt, ppm*	*Conversion of CS_2 to H_2S, %*
1.	50	0.560	0.327	0.887	342	1762	96.0
2.	50	0.580	0.327	0.907	344	1762	96.0
3.	50	0.600	0.327	0.927	345	1762	96.8
4.	50	0.560	0.327	0.887	345	1762	97.2
5.	50	0.336	0.327	0.663	347	1762	96.0
6.	50	0.466	0.327	0.793	347	1762	96.0
7.	50	0.621	0.327	0.948	343	1762	95.2
8.	50	0.224	0.475	0.699	339	1762	90.5
9.	50	0.224	0.327	0.551	349	1762	95.2
10.	50	0.224	0.327	0.551	392	1762	96.6
11.	50	0.224	0.327	0.551	397	1762	96.6
12.	50	0.715	1.290	2.005	397	1762	55.0
13.	50	0.672	1.290	1.962	397	1762	55.3
14.	50	0.715	1.290	2.005	448	1762	59.0
15.	50	0.683	1.903	1.586	397	1762	75.0
16.	50	0.900	1.935	2.835	396	1762	51.9
17.	50	0.896	0.903	1.799	398	1762	71.7
18.	50	0.896	0.903	1.799	398	1762	71.7
19.	50	0.917	0.903	1.820	398	1762	84.3
20.	50	0.194	0.903	1.097	338	3830	51.3
21.	50	0.171	0.903	1.074	383	2880	76.2
22.	50	0.228	0.903	1.131	433	2880	81.1
23.	50	0.139	0.903	1.042	335	1790	58.3
24.	50	0.184	0.903	1.087	337	2800	58.3
25.	50	0.212	0.903	1.115	387	2570	78.9

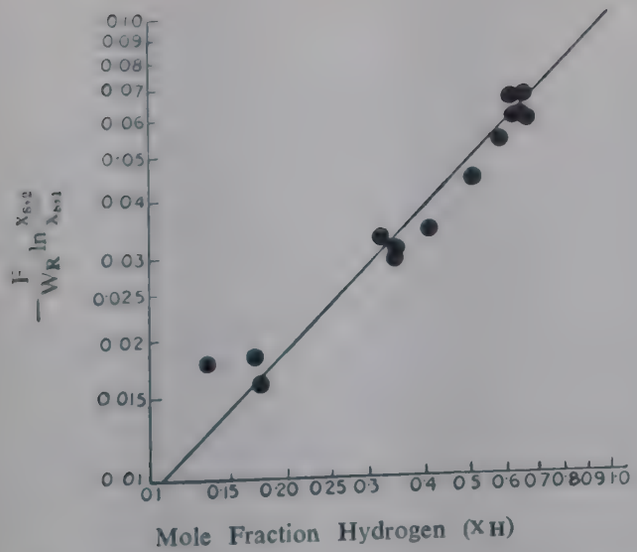

Fig. 2—Effect of Hydrogen Conc. on Rate of Hydrogenation of CS_2 in Heptane Solution in Presence of Cobalt Molybdate Catalyst at 335-350°C and 1 Atm.

molybdate catalyst were used in these experiments.

Application of Theory for Correlating Experimental Data: Since the present series of experiments were carried out under a total pressure of one atmosphere (abs), equation (5) will be simplified to

$$-\frac{F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}} = k_H e^{-E/RT}\, x_H^m \qquad \ldots (6)$$

(since P=1 atm).

To determine the exponent, m, of the above kinetic equation values $-F/W_R \ln x_{s,2}/x_{s,1}$, g. moles/(hr) (g. catalyst), were plotted against x_H, mole fraction of hydrogen, in a log-log graph when a straight-line correlation was obtained (Fig. 2). The exponent, m, was determined from the slope of this straight line and this was found to be unity. Hence the kinetic expression becomes

$$-\frac{F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}} = k_H e^{-E/RT}\, x_H \qquad \ldots (7)$$

Now to obtain the values of E & k_H, an Arrhenius type of plot was made by plotting $\left[-\frac{F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}}/x_H\right]$, g. moles/(hr) (g.catalyst) (mole fraction H_2). against $\frac{1}{T}$, $°k^{-1}$.

A straight-line relationship is obtained from the

TABLE 2—Correlation of Experimental Data

Expt. No.	x_H, mole fraction of hydrogen	$x_{s,1}$; mole fraction CS_2 in feed mixture	$x_{s,2}$ mole fraction CS_2 in Product	$-\frac{F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}}$	$\frac{10^3}{T}$ °K^{-1}	$\ln\left[\left(\frac{-F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}}\right)/x_H\right]$
1.	0.632	0.877×10^{-3}	0.034×10^{-3}	0.0537	1.627	− 2.40
2.	0.640	0.857×10^{-3}	0.033×10^{-3}	0.0548	1.623	− 2.38
3.	0.650	0.833×10^{-3}	0.026×10^{-3}	0.0640	1.620	− 2.30
4.	0.632	0.877×10^{-3}	0.024×10^{-3}	0.0635	1.620	− 2.30
5.	0.507	1.147×10^{-3}	0.045×10^{-3}	0.0427	1.614	− 2.47
6.	0.587	0.970×10^{-3}	0.038×10^{-3}	0.0512	1.614	− 2.43
7.	0.657	0.795×10^{-3}	0.038×10^{-3}	0.0575	1.625	− 2.44
8.	0.320	1.575×10^{-3}	0.150×10^{-3}	0.0329	1.634	− 2.27
9.	0.407	1.370×10^{-3}	0.065×10^{-3}	0.0335	1.610	− 2.48
10.	0.407	1.370×10^{-3}	0.043×10^{-3}	0.0380	1.510	− 2.36
11.	0.407	1.370×10^{-3}	0.043×10^{-3}	0.0380	1.495	− 2.36
12.	0.357	1.490×10^{-3}	0.670×10^{-3}	0.0337	1.485	− 2.36
13.	0.343	1.545×10^{-3}	0.693×10^{-3}	0.0316	1.485	− 2.38
14.	0.357	1.490×10^{-3}	0.610×10^{-3}	0.0360	1.385	− 2.28
15.	0.430	1.320×10^{-3}	0.330×10^{-3}	0.0438	1.484	− 2.26
16.	0.318	1.580×10^{-3}	0.760×10^{-3}	0 0412	1.495	− 2.04
17.	0.497	1.165×10^{-3}	0.330×10^{-3}	0.0440	1.490	− 2.42
18.	0.497	1.165×10^{-3}	0.330×10^{-3}	0.0440	1.490	− 2.42
19.	0.503	1.155×10^{-3}	0.179×10^{-3}	0.0676	1.490	− 1.99
20.	0.177	4.140×10^{-3}	2.010×10^{-3}	0.0160	1.635	− 2.40
21.	0.160	3.170×10^{-3}	0.755×10^{-3}	0.0309	1.525	− 1.64
22.	0.202	3.020×10^{-3}	0.570×10^{-3}	0.0376	1.417	− 1.67
23.	0.133	2.025×10^{-3}	0.850×10^{-3}	0.0182	1.645	− 1.88
24.	0.170	3.050×10^{-3}	1.160×10^{-3}	0.0185	1.638	− 2.21
25.	0.190	2.720×10^{-3}	0.577×10^{-3}	0.0347	1.516	− 1.69

slope and intercept of which the values of E and k_H are found to be 2000 cal./g. mol and 0.532 g.moles/(hr) (g.catalyst) (mole fraction) respectively. Hence the experimental data may be correlated by the following equation.

$$-\frac{F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}}=0.532e^{-1000/T}\,x_H \qquad (8)$$

The values of the functions plotted in Figs. 2 and 3 are shown in Table 2. The effect of space velocity, expressed in terms of g.moles feed (hydrogen+heptane) (hr) (g. catalyst), on per cent conversion of carbon disulphide into hydrogen sulphide is shown in Fig. 4.

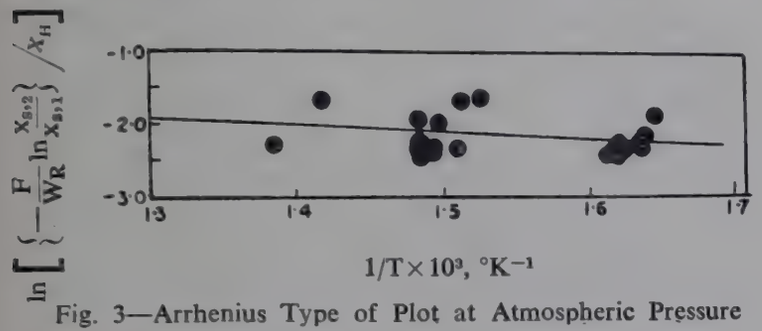

Fig. 3—Arrhenius Type of Plot at Atmospheric Pressure

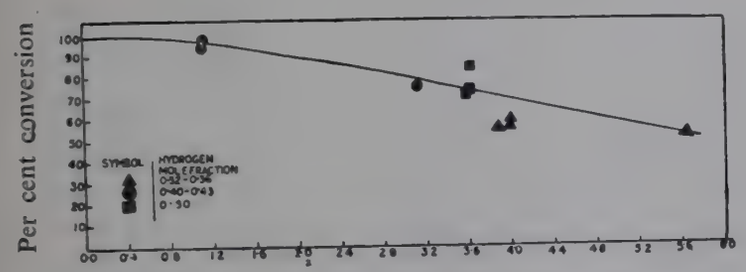

Fig. 4—Effect of Space Velocity on Per cent conversion of CS_2 into H_2S at 392-448°C and Atmospheric Pressure

Discussion

The work was undertaken in connection with the study on steam-naphtha reforming in pilot scale. For this process, organic sulphur in the hydrocarbon should be reduced to 5—8 ppm. Carbon disulphide is one of the many organic sulphur compounds present in naphtha. In the present study, it can be found from Fig. 2 that under atmospheric pressure the allowable space velocity for 99 per cent conversion of carbon disulphide at 335-350°C and 0.5 atm. partial pressure of hydrogen was about 0.0106 g.moles (hydrogen+heptane)/(hr) (g.catalyst). From equation (5) it is found that the space velocity F/W_R, is directly proportional to partial pressure of hydrogen. Hence at hydrogen partial pressure of 10 atm, mole fraction hydrogen 0.5, and temperature 335-350°C, the allowable space velocity for 99 per cent conversion of carbon disulphide may be estimated as 0.212 g.moles (hydrogen+heptane)/(hr) (g. catalyst).

The rate of removal of carbon disulphide in heptane solution, in the present study, may be compared with that of dibenzothiophene in naphtha solution studied by Wilson, Voreck and Malo[10]. The rate equation given by them[10] may be transformed to the form of equation (7) and thus it becomes

$$-\frac{F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}}=\frac{2.2}{1.2}k_s e^{-E/RT},$$

where the value of E for hydrogenation of dibenzothiophene has been given as 3800 g.cal/mole and k_s the velocity coefficient as 1.81 at 11.4 atm. hydrogen partial pressure. Assuming k_s is proportional to partial pressure of hydrogen in accordance with equation (5) above and substituting $k_H p_H$ for $(2.2/1.2)k_s$, the following equation is obtained for removal of debenzothiophene

$$-\frac{F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}}=k_H e^{-3800/RT}\,p_H=k_H e^{-1900/T}\,p_H.$$

Now since $k_s=1.81$ at pH=11.4 atm.

$$\therefore k_H=\frac{2.2}{1.2}\times\frac{1.81}{11.4}=0.29,$$ g.moles/(hr). (g. catalyst) (atm H_2 pressure)

Hence the equation for dibenzothiophene removal becomes

$$-\frac{F}{W_R}\ln\frac{x_{s,2}}{x_{s,1}}=0.29e^{-1900/T}\,p_H=0.29e^{-1900/T}\,x_H$$

at one atm. pressure. Comparing this equation with the rate equation, viz. equation (8), for carbon disulphide removal, it is found that for the same per cent conversion at 350°C and same partial pressure of hydrogen, space velocity F/W_R for dibenzothiophene removal would be about 7.83 times less than that for sulphur removal from carbon disulphide.

Nomenclature

- e = Constant, 2.72.
- E = Energy of activation, calories/g.mol.
- F = Total feed, g.moles (hydrogen+ hydrocarbon)/hr.
- F_H = g.moles hydrogen/(hr)
- F_{HC} = g.moles hydrocarbon/hr
- k_H = velocity coefficient, g.moles/(hr). (g.catalyst) (mole fraction H_2)
- m = exponent on partial pressure of hydrogen
- P = total pressure, atm.
- p_H = partial pressure of hydrogen, atm.
- p_s = partial pressure of sulphur compound, atm.

R = gas constant, 1.987 g.cal/(g.mole) (°K)
T = absolute temperature, °K
V_H = velocity of hydrogenation of organic sulphur compound, $\frac{\text{g. moles}}{\text{(hr) (g. catalyst)}}$
W_R = weight of catalyst, g
x_H = mole fraction of hydrogen
x_s = mole fraction of sulphur compound
$x_{s,1}$ = mole fraction of sulphur compound at inlet to the catalyst bed
$x_{s,2}$ = mole fraction of sulphur compound at outlet from the catalyst bed

Acknowledgements

The authors acknowledge the valuable assistance rendered by Sri K. P. Rao during the preparation of the catalyst. Their thanks are also due to Dr. K. R. Chakravorty, General Manager, for his active interest in this work. Sri Tinkari Banerjee, Operator, assisted us throughout the experimental part of this work.

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Characterisation of Fused Iron Catalyst for Ammonia Synthesis. Part I: Differential Thermal and X-Ray Diffraction Analyses

By

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Different samples of fused iron catalyst for ammonia synthesis have been investigated by differential thermal and x-ray diffraction techniques. DTA thermogram and x-ray pattern of these samples reveal the presence of magnetite in each of them, but they differ from both natural and synthetic magnetite in finer details. The above feature of catalyst samples has been attributed to the presence of promoter ions in their body structure.

The major phase of the different varieties of fused iron catalyst, used extensively for ammonia synthesis, is magnetite. The active state of this catalyst is, however, obtained by reducing it with hydrogen or a mixture of hydrogen and nitrogen in the converter before use for the synthesis.

As a fused iron catalyst usually promoted with various oxides, like K_2O, Al_2O_3, CaO and MgO, it is likely that there will be some sort of substitution in the magnetite matrix. In fact microscopic examination of such a catalyst reveals that oxides of alkaline earth metals appear to enter in the magnetite matrix

easily[1], and the presence of these oxides leads to higher solubility of other promoters in the matrix. Again, the distribution of these promoters in the magnetite matrix is also influenced profoundly by their ionic radius as well as annealing process of this catalyst in molten state[2].

Differential thermal analysis has been utilized to characterize magnetite[3,4]. Magnetite shows two exothermic peaks[5] in its DTA diagram, but the peak temperature varies according to its mode of formation[6]. In case of synthetic sample[5], these peaks are in the region of 275-350°C and 590-650°C, whereas in natural varieties these occur in the region of 350-400°C and 600-1000°C. According to Schmidt and Vermaas[4], the first exothermic effect is due to oxidation of surface layer of the magnetite, whereas the second effect is due to slow oxidation of the remainder of the magnetite and commences once the structure has opened up after the Curie point. As substitution of different ions in the magnetite lattice influences its structure, DTA study of the fused iron catalyst samples may indicate some features regarding their structural characteristics with respect to the substitution effect of promoter ions on the matrix of magnetite.

Keeping that in view attempts have, therefore, been made to elucidate structure of some fused iron catalyst samples having different promoter ions in their body composition and being usually used at different pressure and temperatures for ammonia synthesis.

Experimental

The following catalyst samples were studied, viz. samples I, II, III and IV. Sample I is used at a pressure of about 200 atm. and a temperature of about 450°C whereas the rest are used at about 450 atm. and 600°C. Sample I was collected from the Sindri Unit and all the rest from the Nangal Unit of FCI Ltd. Samples I and III were promoted with Al_2O_3, CaO and K_2O, while II with Al_2O_3, MgO and K_2O and IV with Al_2O_3 and K_2O only. Their chemical composition is given in Table 1.

TABLE 1—Chemical Composition of Fused Iron Catalyst Samples for Ammonia Synthesis

	Sample No.			
%	*I*	*II*	*III*	*IV*
Fe_2O_3	57.65	68.85	71.80	69.79
FeO	33.76	22.50	22.45	24.12
Al_2O_3	4.84	4.82	3.24	4.78
CaO	2.21	Nil	2.18	Nil
MgO	Nil	3.18	Nil	Nil
K_2O	0.70	0.60	0.78	1.10
Total	99.16	99.95	100.45	99.79

DTA investigation was carried out in a manually operated apparatus fabricated in this laboratory. α Al_2O_3 was used as the reference substance. Chromel/alumel thermocouple was utilized for this investigation. The rate of rise of temperature of the furnace was maintained at 10°C/min. by a manually operated variable autotransformer. Sample holders in cylindrical shape were made of thin platinum sheet.

DTA results of the catalysts and of a naturally-occurring magnetite sample are shown in the Table 2 and thermograms in Fig. 1.

FeK_α radiation generated by 30 KV and 10 mA in a Philips PW 1010 unit and a Debye-Sherrer camera of 57.3 mm. diameter have been used for the x-ray diffraction study (Table 3, Fig. 2). The time of exposure was 5 hours. Crystal size of the magnetites

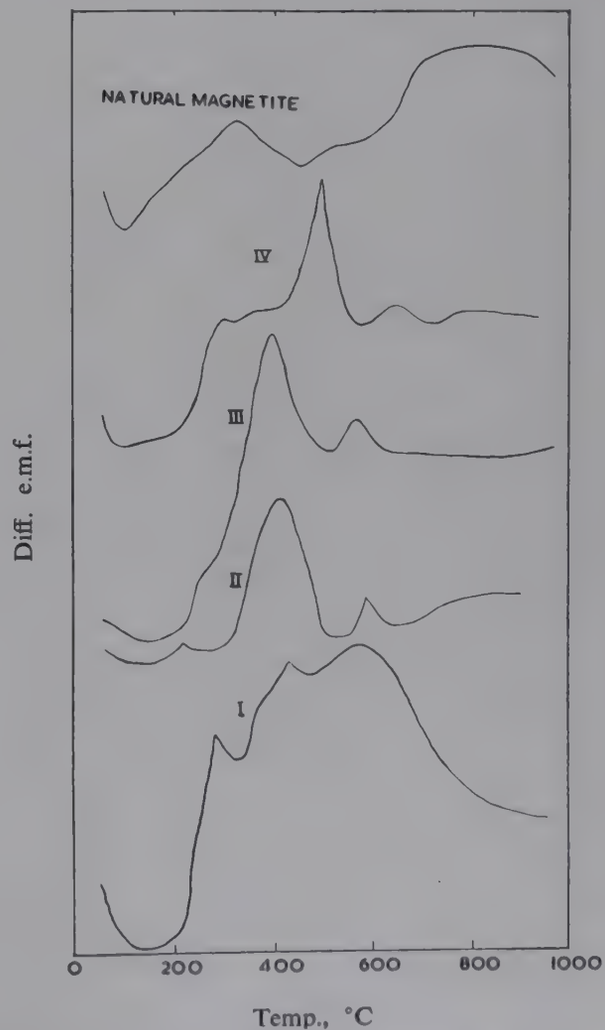

Fig. 1—DTA curves of catalyst samples and a Natural Magnetite

TABLE 2—Temperature and Nature of Peaks of the Ammonia Synthesis Catalyst Samples

Sample No.	*Peak Temperature, °C Exothermic*
I	280 weak 430 weak bulge 560-570 strong
II	240 weak 420 strong 590 medium
III	240 weak bulge 400 strong 580 medium
IV	300 weak 500 strong 640 medium
Natural Magnetite	350 medium 700-900 strong bulge

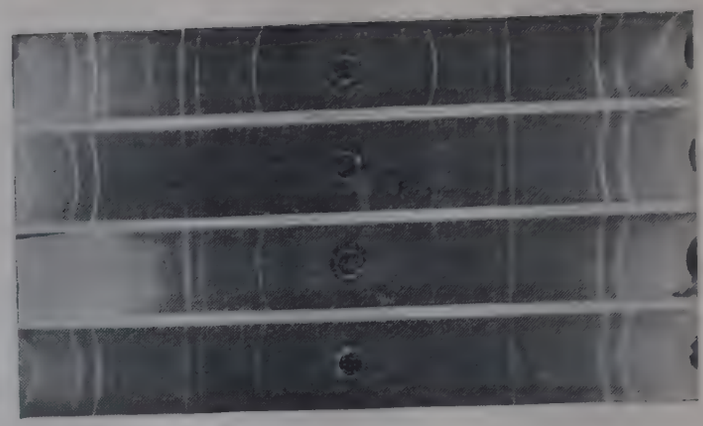

Fig. 2—X-ray Diffraction Pattern of Catalyst Samples

has been measured from the broadening of their high angle line (d_{440}) using the following equation[5].

$$\beta = \frac{C\lambda}{t \cos \theta_{hkl}}$$

where β = line broadening = B-b.
b = breadth of line of the quartz crystal having $> 10^{-5}$ cm. diam.
B = breadth of line of test sample.
C = 0.89.
λ = Wave length of X-radiation.

TABLE 3—X-ray Data of Fused Iron Catalyst Samples for Ammonia Synthesis

Sample No								*Standard data*					
I		II		III		IV		*Magnetite*		Fe_2O_3		*FeO*	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
4.80	F	—	—	4.81	F	—	—	4.85	10				
—	—	—	—	3.66	VF	—	—	—	—	3.67	35		
2.960	M	2.940	M	2.970	M	2.965	M	2.97	30	—	—		
—	—	2.692	VF	2.698	F	2.688	F	—	—	2.69	100		
2.555	S	2.530	S	2.535	S	2.531	S	2.532	100	2.514	75		
2.148	F	—	—	—	—	—	—	—	—	—	—	2.145	100
2.104	M	2.096	M	2.109	M	2.101	M	2.101	20	—	—	—	—
—	—	—	—	1.849	VF	1.843	VF	—	—	1.838	30	—	-
1.724	M	1.172	M	1.718	M	1.714	M	1.714	15				
—	—	1.697	VF	1.700	VF	1.697	VF	—	—	1.692	45		
1.624	M	1.615	M	1.620	M	1.617	M	1.617	25				
1.526	VF	—	—	—	—	—	—						
1.489	S	1.482	S	1.488	S	1.485	S	1.485	35			1.515	
—	—	—	—	—	—	1.457	VF			1.452	25		
1.352	F	1.325	F	1.336	VF	1.326	VF	1.327	6				
—	—	—	—	1.315	VF	1.313	VF	—	—	1.310	10		
1.299	VF	—	—	—	—	—	—	—	—			1.292	25
1.285	M	1.280	M	1.284	M	1.281	M	1.280	10				
1.271	F	1.265	F	—	—	—	—	1.266	3				
1.217	F	1.211	F	1.218	F	1.214	F	1.212	4				
1.097	M	1.093	M	1.097	M	1.094	M	1.093	15				
1.054	F	1.049	F	1.053	F	—	—	1.050	4				

Where S— strong, M— medium, F—faint and VF—very faint, d—interlayer spacing (Å) and I—relative intensity.

t = size of the crystal.

θ_{hkl} = Bragg angle of line d_{hkl}

Breadth of the line was taken at the half maximum intensity in the intensity vs. θ_{hkl} diagram of the line. The results were shown in Table 4.

TABLE 4—Crystal Size of the Magnetites of Fused Iron Catalyst Samples

Sample No.	*Size of the Crystal* (Å)
I	387
II	590
III	630
IV	391

Discussions

DTA curves of the samples reveal two distinct oxidation peaks in the region 400-500°C and 570-650°C which are similar to that of magnetite (vide Table 2 and Fig. 1), but differing in finer details. There is one weak exothermic peak at 240-300°C in each case, but no such peak is observed in the DTA diagram of natural magnetite (Fig. 1). Again, their peak temperature due to first oxidation is higher in each case than that of the natural magnetite. This is more pronounced in sample IV where deviation is quite appreciable. With respect to the peak temperature of the second stage of oxidation, it is observed that those of three samples, viz. I, II and III are lower than that of magnetite, while that of sample IV corresponds satisfactorily to that of the natural magnetite. The appearance of a new peak as well as changes in the position of peaks in the case of catalyst samples may be attributed to the presence of different promoter ions in the magnetite lattice.

X-ray study (vide Fig. 2 and Table 3) of all fused iron catalyst samples reveals the presence of magnetite in each case. Besides this, some lines due to αFe_2O_3 are found in the x-ray pattern of samples II, III and IV, whereas very faint lines due to FeO (d-2.148, 1.526 & 1.299Å) are present in sample I.

Again, it has been observed that the crystal sizes of these magnetites are within the range of 387-630Å, but when they are compared among themselves, it is found that the particle size of samples I and IV is finer than that of II and III (Table 4). Evidently this may be attributed to the difference in the method of preparation and annealing process of the catalyst samples.

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Characterisation of Fused Iron Catalyst for Ammonia Synthesis. Part II—Magnetic Studies

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A few different types of ammonia synthesis catalysts have been studied magnetically. From the saturation moments, it is found that the promoter ions, like Al^{3+}, Ca^{2+} and Mg^{2+}, enter the magnetite lattice, which is the major constituent. It has been observed that Mg^{2+} enters both octahedral and tetrahedral intersticial sites, the others entering only the octahedral ones. K^{+} ions are found to form both ferromagnetic and diamagnetic compounds which do not enter the magnetite lattice.

It is well known that ammonia synthesis reaction is catalysed by finely divided iron, which is usually formed by reducing magnetite in the reaction bed. The catalytic action is enhanced by the presence of certain substances added to the magnetite as promoters. These promoters, e.g., Al_2O_3 in this case, themselves may sometimes catalyze the reaction, but their main purpose perhaps is to modify the structure of the catalyst in a way to increase the activity of the latter. Certain varieties of ammonia synthesis catalysts, in which Al^{3+}, Ca^{2+}, Mg^{2+} and K^{+} ions are used in different proportions as promoters, are studied magnetically. These have been also studied by Mukherjee[1] et al, appearing elsewhere in this issue, employing techniques like differential thermal analysis, x-ray diffraction and chemical analysis. The object of the present work is to investigate into the structural changes in the magnetite lattice induced by the presence of the promoters and thermal treatment.

Magnetite has an inverse spinel structure represented by Fe^{3+} $(Fe^{2+}$ $Fe^{3+})$ O_4^{2-}, where the cations written within the parentheses occupy octahedral interstical positions in the face centred cubic oxygen lattice, and the remaining Fe^{3+} ions outside the parentheses occupy tetrahedral interstices. Néel[2] suggested that the ions form two different sub-lattices, with spins aligned in opposite directions, so that the spin moments of the two types of Fe^{3+} ions cancel one another, leaving the Fe^{2+} ions responsible for the magnetic properties. The observed Bohr-magneton number of 4.2 supports this hypothesis. According to Néel, replacement of an iron ion by a non-magnetic ion at an octahedral interstice will result in a decrease in the specific magnetization at saturation, whereas replacement at a tetrahedral site will result in an increase. The results of Gorter[3] confirmed the hypothesis. Thus, by measuring the specific magnetization, the type of sites at which the promoter ions may have entered the magnetite lattice can be determined.

Another aspect of magnetic studies is the thermomagnetic analysis, where isolated ferromagnetic components in a multi-component system can be identified by their characteristic Curie temperatures, at which the ferromagnetism of the components disappears resulting in a sharp decrease in the magnetic moment.

A decrease or increase in magnetic moment may also accompany a phase change, so that from magnetic data alone it is sometimes difficult to distinguish between a Curie-point transition and a phase change except in case of very well-known transitions. Differential thermal analysis can sometimes be of help in case of the previously unknown or less known transitions, as Curie points are always shown as endothermic peaks there, whereas phase changes may be recorded

as either endothermic or exothermic peaks.

In the promoted iron Fischer-Tropsch Catalysts, a peculiar transition point was observed at about 250°C by Leclerc and Lefebvre[4], who ascribed it to the Curie-point transition of the saturated solid solution of K_2O in γ-Fe_2O_3. Their conclusion was based on a publication by Michel and Chaudron[5] who, however, subsequently stated[6] that the Curie point of this phase is at 630°C. The inference of Leclerc and Lefebvre is thus left open to doubt. Similar transition in the range 150°-250°C is observed in the catalysts studied here, and has been investigated in some details. The possibility of formation of potassium ferrite, $K_2Fe_2O_4$, has been considered.

Finally, if a ferromagnetic substance forms a solid solution with any other substances—ferromagnetic or otherwise—its Curie point shifts from its original value, solution with a non-ferromagnetic substance always resulting in a lowering of Curie point. The lattice parameters also change on solid solution formation, so that there is a possibility of correlating lattice parameter with the Curie point. Such a correlation is indeed possible for simple two-component systems. Thus, Poulard[7] reporting on Fe_3O_4-Al_2O_3 system, where Al^{3+} replaces Fe^{3+} in magnetite, observes a lowering of lattice parameters with increasing Al^{3+} concentration. Burdese and Brisi[8], on the other hand, find that for Ca^{2+} substituted magnetite, the lattice parameters increase with increasing Ca^{2+} concentration. In both these cases the Curie point is progressively lowered. So, in multicomponent systems, Curie point cannot be easily correlated with lattice parameters.

Experimental

Measurements were taken on a modified Curie-type magnetic balance comprising a horizontal light silica beam kept under taut suspension from two vertical medium-fine phosphor bronze strips. At one end of the beam a platinum sample container is attached. This end enters a non-inductive horizontal electric furnace giving temperatures up to 1000°C. The furnace is kept in the field of an electromagnet. The field direction is vertical, and a specially shaped pole-shoe after the design of Sucksmith[9] introduces a horizontal field gradient, perpendicular to the balance beam. The force on the sample is balanced by passing an electric current through a rectangular coil of enamelled copper wire wound on a perspex frame fixed to the other end of the balance beam. The coil moves in the field of a powerful permanent magnet. The balancing current is read off an accurate milliammeter, provided with shunts to give different ranges.

Temperature is measured by a chromel-alumel thermocouple, one junction of which is kept near the sample, the other maintained at 0°C.

The null position of the balance is determined by reflecting a beam of light off a mirror attached to the balance beam on two barrier layer type photo-electric cells connected in opposition. A deflection in the beam causes the unbalanced photo-current to produce a large deflection in a critically damped sensitive galvanometer.

For the saturation specific magnetization measurements, a magnetizing current of 4 amp. was used in the electromagnet, corresponding to about 3,000 oersteds. The samples were found to attain saturation at this field strength. The gradient at this field strength is about 10 oersted/cm at centre.

For the Curie point determination, a very low field was used, as the use of high fields tends to obscure the sharpness of the transformations as observed by Hofer and Cohn[10]. The samples were heated from room temperature up to 800°C at the rate of 20°C/min. approximately. This fast rate of heating was chosen to minimize oxidation effect.

The catalyst samples were broken into small lumps of about 2-3 mm. in size for accommodating in the sample container and one single lump, as nearly spherical as possible was chosen in each case. To eliminate the effect of the water-soluble potassium salts, the samples were powdered, thoroughly leached with water, dried at 100°C and measured. Thus, two different thermomagnetic curves were obtained for each catalyst sample.

To investigate the effect of potassium ferrite, $K_2Fe_2O_4$ was prepared by fusing α-Fe_2O_3 with KOH at 1000°C and the resulting mass was examined thermomagnetically (Fig 1) and by D.T.A. Natural magnetite

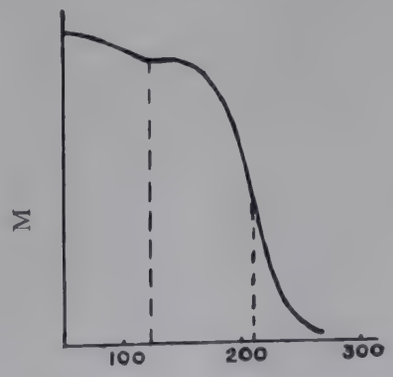

Fig. 1—Thermomagnetic curve for $K_2Fe_2O_4$

(M stands for Magnetic moment)

was also studied (Fig 2) for comparison with the catalyst samples.

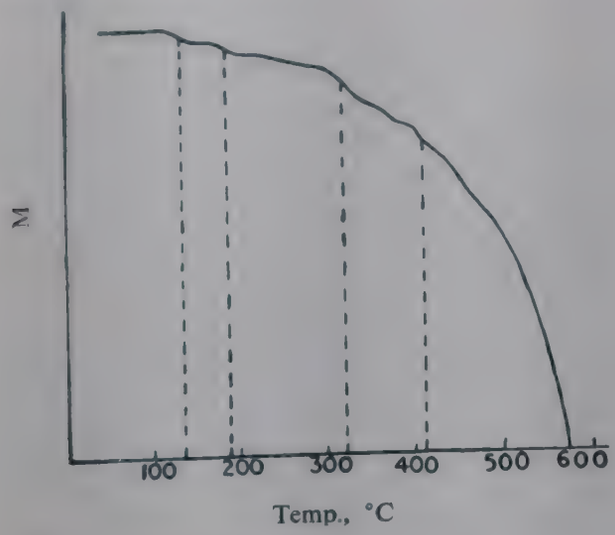

Fig. 2—Thermomagnetic curve for natural magnetite

In the thermomagnetic analysis, all the samples were subjected to heating from room temperature up to the maximum, subsequently cooling down to room temperature in order to determine any possible thermal hysteresis and the extent of oxidation.

Results

The specific magnetization values of the different samples, together with their chemical composition are given in Table 1. Spectroscopically pure iron was used for calibration, its specific saturation magnetization at room temperature being taken as 218.

Reproduced below are the thermomagnetic curves showing the variation in the magnetic moment M with temperature for the samples as they are, as well as for the leached samples (Figs. 3, 4). The solid curves are obtained when heating the samples from room temperature, and the broken curves when cooling down.

Discussions

All the catalyst samples exhibit Curie temperatures below 540°C.

Burdese and Brisi[8] reported a similar depression of Curie point of Fe_3O_4 on formation of solid solution

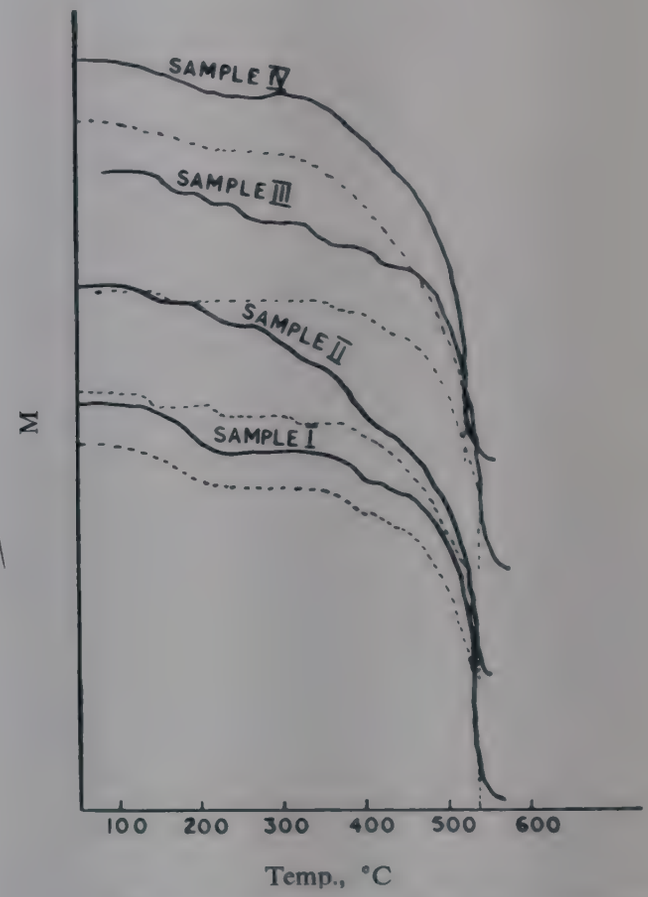

Fig. 3—Thermomagnetic curves for the unleached catalysts

TABLE 1—Specific Saturation Magnetization Values

Sample No.	Composition, %						Sp. Sat. Magnetization	
	Fe_3O_4	FeO	Al_2O_3	CaO	MgO	K_2O	Normal Samples	Leached Samples
I	57.65	33.76	4.84	2.21	—	0.70	88	84
II	68.85	22.50	4.82	—	3.18	0.60	96	97
III	71.80	22.45	3.24	2.18	—	0.78	111	82
IV	69.79	24.12	4.78	—	—	1.10	85	94
V	Natural Magnetite		—	—	—	—	105	—

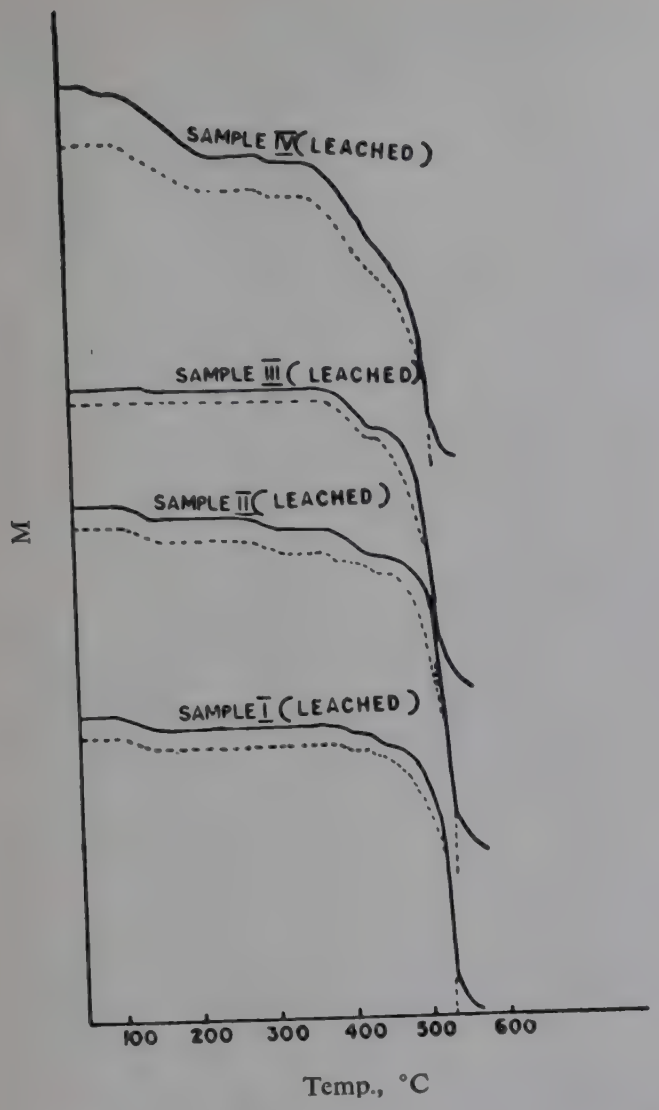

Fig. 4—Thermomagnetic curves for leached catalysts

with Fe_2CaO_4. Part of their results is summarised below:

Mol Fe_2CaO_4 %	*Lattice parameter*	*Curie temp., °C*
1.0	8.394	565
5.5	8.414	520
12.0	8.444	445

The data on the specific saturation magnetization of the catalyst samples give information regarding the nature of the lattice substitution. For this purpose, the data on the leached samples have been considered as they are free from the effect of the soluble potassium salts which do not enter the magnetite lattice. The value for the specific saturation magnetization of natural magnetite at room temperatures is found to be 105. As against this, the value for sample IV, where the only possible substitution is by Al^{3+}, is found to be 94. The Al^{3+} ions have obviously entered the octahedral interstices. In samples I and III, where calcium is used as a promoter, the specific saturation magnetization values are 84 and 82 respectively, showing that the Ca^{2+} ions also enter the octahedral sites, as expected.

Sample II, containing Mg^{2+} instead of Ca^{2+}, may be expected to have a magnetization value similar to the Ca^{2+} substituted ones, but here the measured value is 97, i.e. almost identical with the simple Al^{3+} substituted catalyst. There are two alternative explanations for this: Mg^{2+} may not have entered the magnetite lattice at all, but remained as magnesium aluminate; or it may have entered both the octahedral and the tetrahedral sites, thus causing the fall in magnetization in one being compensated by rise in the other. The x-ray diffraction studies[1] have failed to show up the presence of any magnesium aluminate, so it seems that the alternative explanation is the more probable one. Normally Mg^{2+} goes to the octahedral sites. But the presence of Al^{3+} already in some octahedral sites may have induced part of the Mg^{2+} ions to move to the tetrahedral sites. Gorter[3] had observed a similar effect with Zn^{2+}. In case of magnetite simply substituted by Zn^{2+}, the zinc ions occupy the octahedral sites, but for doubly substituted magnetite, Zn^{2+} is found to move over to the tetrahedral sites.

Another interesting aspect is the presence of the potassium salts. In sample IV, there was no remarkable difference between the nature of the thermomagnetic curves of the leached and the unleached samples. But the specific magnetization of the leached sample is the higher of the two. We may conclude thereby that the potassium salt present here was a diamagnetic one.

In sample II, the specific magnetization is practically unchanged on leaching, but the nature of the thermomagnetic curve has changed considerably. The curve for the leached sample is much sharper and one ferromagnetic phase with its Curie point near 210°C is found washed out. This ferromagnetic phase has been shown as $K_2Fe_2O_4$. D.T.A. of synthetic $K_2Fe_2O_4$ has been performed up to 400°C and only one endothermic peak at about 210°C has been observed as expected. Thus, potassium exists here in this form to a small extent, and to a much larger extent in a diamagnetic form.

Similar observations were made in case of samples I and III; only in these the ferromagnetic $K_2Fe_2O_4$ is present in larger quantities, being the maximum in sample III.

Removal of $K_2Fe_2O_4$ results in a "sharper" thermomagnetic curve, in which the different small changes are displayed more prominently. A similar sharpness is observed in the cooling curves of the unleached samples. The lack of sharpness can be then attributed to the slow oxidation of $K_2Fe_2O_4$.

It may therefore be concluded that the natures of substitution by Ca^{2+} and by Mg^{2+} are different and we may expect somewhat different degrees of efficiencies for the two.

Acknowledgements

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On the Interaction of Ammonia and Soil Humic Acid in Presence of Ammonium Sulphate

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It has been observed that a given quantity of soil humic acid requires a larger amount of ammonium hydroxide to attain a particular pH in presence of ammonium sulphate than in its absence. This result has been explained on the basis of the electrical double-layer theory.

Humus is a natural body consisting of a mixture of groups of chemical complexes. Although there is a wide variation of its composition and in fact no two samples collected from different places of the earth are alike, yet they show some common and characteristic properties. The exact nature of these substances is not yet known. Waksman and Gillam[1] found evidence that lignin-like substances are present in humus. The cation-exchange property is believed to be due to the acid ionisation of the residual COOH and phenolic OH groups.

Several workers have investigated humic acid by electrometric titration methods[2–7]. Sen[2] investigated the effect of the different constituents of soil humic acid in the formation of clay-humus complexes by potentiometric titration as well as by analytical methods. Chatterjee[3] studied the electrochemical properties of humic acid and believes that humic acid sols contain weakly dissociated acids, part of which is in true solution and part consists of insoluble colloidal particles. He observed that the base-exchange capacity of the sols depends on the nature of the base used for titration

and the results can be explained on the basis of Mukherjee's theory of electrical double layer and secondary adsorption[8]. In the light of this theory, Mukherjee et al interpreted the results of their experiments on the base binding capacities of hydrogen clay both in presence and in absence of neutral salts[9,10]. This paper deals with the interaction of ammonia and soil humic acid in presence of ammonium sulphate and the results are explained by the above theory.

Experimental

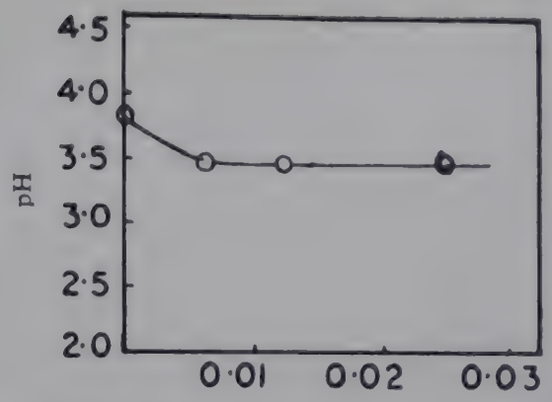
Humus from the surface layer of a sample of black cotton soil was treated with approximately 0.5 N Na_2CO_3 solution. Hydrochloric acid was added to the extract till the pH was 2.0-3.0 and crude humic acid was precipitated. The precipitate was dissolved in sodium carbonate solution, reprecipitated and separated from the supernatant liquid with the help of a centrifuge. The process was repeated for a number of times and then finally electrodialysed till it was free from electrolytes. The humic acid sol thus obtained was made up to a 0.2 per cent suspension. The ash content was about 5 per cent.

The potentiometric titrations were carried out in a Cambridge pH meter, for which 10 ml of ammonium sulphate solution of the requisite concentration were added to 10 ml of the humic acid solution. After thorough mixing, the mixture was kept in a thermostat maintained at 25°C for 1 hour and then titrated with 0.04 N NH_4OH. The same titration was then repeated after keeping the mixture of humic acid and ammonium sulphate in the thermostat for 5 hours and the titration was found to be reproducible within the limit of experimental error. This indicates that the mixture attains equilibrium within a short time. Ammonium sulphate was of AnalaR (B.D.H.) quality.

Any change in pH due to hydrolysis of ammonium sulphate was determined previously by comparing the pH of the blank aqueous solutions of ammonium sulphate having the same concentrations used in the experiment.

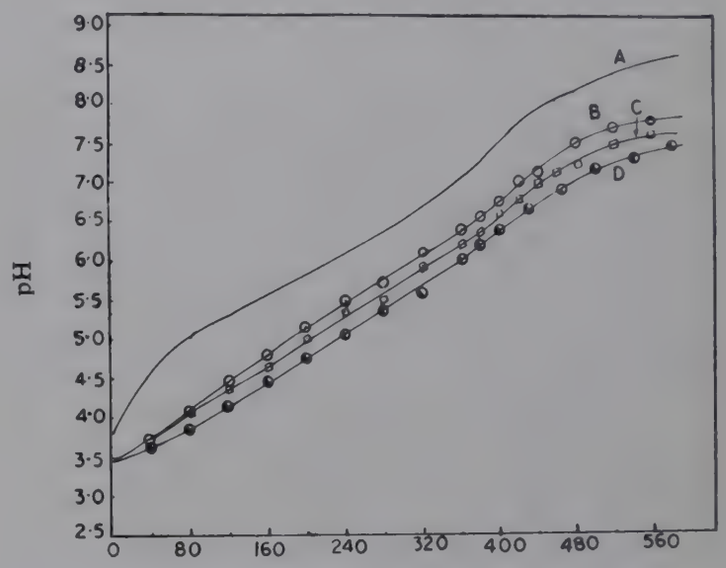
Discussions

It will be evident from Fig. 1 that addition of ammonium sulphate (0.0062 M) to humic acid causes a lowering of pH from 3.87 to 3.45 but further addition does not lower the pH any more. Moreover, it will be observed from the curves B, C and D in comparison to A, that the height of titration curves gradually shortened due to the presence of increasing amounts of ammonium sulphate (Fig. 2). This means that in



Conc. of $(NH_4)_2 SO_4$ in Humic Acid, moles/1.

Fig. 1



Base/100g., m.eq.

Fig. 2

A—Humic Acid (HA) Alone
B—HA in 0.0062N $(NH_4)_2 SO_4$
C—HA in 0.0125 M $(NH_4)_2 SO_4$
D—HA in 0.025 M $(NH_4)_2 SO_4$

the presence of more ammonium sulphate, a given quantity of humic acid requires more ammonia to attain a particular pH.

The curves show the weak acidic character of humic acid. One faint deflection is observed in each case. A similar observation was made by earlier workers[2,3]. The probable explanation is that humic acid contains mixture of acids of slightly different dissociation constants.

Mukherjee[9] et al observed that neutral salts liberate considerable quantities of acid from the clay acids. They explained their results from the point of electrical adsorption of ions. Since humic acid behaves almost

like clay acids in base-exchange reactions, the above theory has been applied to the present study. The colloidal humic acid particles may be regarded to be surrounded by hydrogen ions existing partly in a free condition forming the mobile electrical double layer and partly in the secondarily adsorbed state on the surface. The free or osmotically active hydrogen ion is responsible for the observed hydrogen activity of the sol. The remaining hydrogen ions are in bound state that is osmotically inactive. Now when ammonium sulphate is added, its cations displace hydrogen ions from the double layer, that is, electrically adsorbed hydrogen ions, resulting in a decrease in pH. But more additions of ammonium sulphate do not cause further displacement of hydrogen ion from the double layer and hence pH remains practically same (Fig. 1). This indicates that only a certain fraction of ammonium ions from the salt added, can take part in the adsorption. In the absence of ammonium sulphate, the addition of ammonium hydroxide to humic acid causes at first the neutralization of mainly mobile hydrogen ions and the pH rises. The equilibrium between mobile and bound hydrogen ions is shifted and more hydrogen ions pass from the double layer to the mobile condition which are then neutralized. In this process the pH gradually rises (curve A of Fig. 2).

In presence of ammonium sulphate, when free base ammonium hydroxide is added to humic acid, at first neutralization of mobile hydrogen takes place and equilibrium is thus shifted; at the same time the unreacted cations, which have not taken part in the adsorption and present in large number, as well as those from free base displace hydrogen ions from the double layer into a neutralizable condition. Hence the total amount of neutralizable hydrogen is increased in presence of ammonium sulphate. Therefore a given quantity of humic acid will require more amount of ammonium hydroxide to attain a particular pH in presence of ammonium sulphate, and the concentration of the latter plays a predominant role in the process. Thus, in order to explain the behaviours of humic acid a different theoretical treatment, from that of acids in true solution, is necessary.

Ammonia is known to be adsorbed directly by the soil[11] and humus[12]. As shown above, the adsorption is greater in presence of ammonium sulphate. It is profitable to see if ammonia adsorption from atmosphere is increased in presence of ammonium sulphate.

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Energy Field of the Universe and Atom Parts II & III

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*Synopsis**

In this work† the theory of tetrahedral dimensional configuration of universal spherical wave has been enunciated. The theory, as a single unified concept, is of universal applicability which is capable of explaining various manifestations in the Universe covering both inanimate and animate fields. Its significance lies not only in its applicability to explain modern scientific observations but also in bringing to light discrepancies in the conventional basic approaches in modern science. The theory opens up new avenues for investigation of problems in various disciplines of science which have remained obscure so far. Thus, it provides explanations and reveals relevant limitations in various scientific postulates propounded by renowned scientists from Newton to Einstein. The basic concepts involved in statistics of Maxwell-Boltzman, Bose-Einstein and Fermi-Dirac; Heisenberg's principle of uncertainty; conventional understanding of the phenomena of gravitation and electromagnetism; the dimensional significance of fundamental constants in modern science; the basic concepts in kinetic theory and thermodynamics; synthesis and annihilation of matter; the recent theory proposed by Hoyle and Narlikar as also the phenomenon of the Ikeya Seki comet observed recently in October 1965, have been discussed.

In dealing with science in ancient India in Part III, the present postulates have been shown to be similar, if not identical, in approach with the Sankhyya postulates of Kapila. The similarity between the basic postulates of Sankhyya with those of the present theory have been shown.

The present theory explains diverse modern scientific observations of phenomena or concepts capable of independent existence in equilibrium. An attempt has been made to show how in ancient India the application of the basic Sankhyya postulates also resulted in the evolution of various disciplines of science, such as astronomy, astrology, evolution of numbers, geometry, trigonometry, concept of Zero and infinity, decimal and octave systems, evolution of language and scripts (viz. *Maheswari*, *Brahmi* and *Devanagri*), evolution of the symbols like *Swastika* and *OHM*, significance of the dancing pose of *Nataraja*, the evolution of musical sound and scale.

Ayurvedic system of diagnosis and treatment of disease, and the concept of *Brahma Tanmatric* field of *Indriya Atmic* consciousness, leading to the enunciation of the *Dvaita* and *Advaita* equilibrium states of Absolute *Paramatmic Dimension* have been explained in the light of this theory.

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* This is in continuation of the Synopsis of the Part I, *Technol* **1** (1964), 3, 19.

† 1. Energy Field of the Universe and Atom Part II: The Theory of Universal Spherical Wave and Modern Science, *Technol* **1** (1965), 4, Spl. Issue.

2. Energy Field of the Universe and Atom Part III: The Theory of Universal Spherical Wave and Science in Ancient India, ibid. Spl. Issue.

Present Theory and Modern Science

The basic ideas which led to the development of the theory of spherical wave of energy field of the Universe were first developed in two previous papers, viz. 'Thermodynamics and External Agency' (1963)†, and 'Variable velocity of light and its influence on matter, energy, space, gravitation and universal equilibrium'.** The former has dealt with the case that no 'action' is possible in the universe without the aid of or without being caused by a potential due to a fundamental dimension. The delineation of the question of Energy as fundamental and Matter, Space and Time etc. as derived dimensions in the present work was deduced on the basis of this

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† Unpublished work

** *Technol*, 1 (1964), 1, 2

finding. In the latter, it has been shown that the velocity of radiation cannot be constant in the universal context, if the inanimate universe, whatever might be its magnitude, has to have a finite configuration capable of independent existence. Because of the variability associated with the dimensions, constitution of the Universal energy field and the phenomena of acceleration and retardation have to play their part.

From these, it has been deduced that the inanimate Universe is an independent equilibrium entity of four dimensions comprising of two opposite pairs of two opposites, namely, Energy, Matter, Space and Time associated with variability leading to a tetrahedral dimensional configuration of the spherical wave of energy field. Further, the law as a single unified concept has been shown to explain manifestations capable of existing as an independent equilibrium entity of four dimensions varying between two opposite pairs of two opposites establishing the equilibrium assuming tetrahedral configuration is expressed as

$$\frac{+}{-} = \frac{-}{+} \text{ or } \frac{(+)\ (+)}{(-)\ (-)} = [\,f\,].$$

This with usual dimensions in inanimate Universe would be presented as $ET/LM=f$, where f can assume any value between zero and infinity; when $f=1$, all four dimensions assume equal magnitudes depending on the nature of variability in the states of existence in homogeneous or heterogeneous phase.

The postulates bring to light the actual significance of time in terms of space in a configuration in which space is radial and time is orbital and differentiate between the significance of matter as momentum or energy and the elementary matter as atomic mass; the theory also brings out the limitations in the definition of Euclidean concept of a point and its position, implications of static and dynamic configurations and distinguishes between the direction and dimension, magnitude of *number of units* and magnitude of potential of a unit, and explains the mechanism of creation of space by the potential of fundamental dimension as energy and contraction of time in space configuration due to derived dimension as elementary matter.

The theory clarifies the significance of radial space and equipotential time in configuration, the radial evolution being four dimensional in space and the equipotential evolution three dimensional in time; the former is tetrahedral and the latter is described by rectangular coordinates.

The theory reveals our limitation in physical perception of a total concept and distinguishes between homogeneity and heterogeneity, space and vacuum, energy and matter creating space and time orbit in spatial configuration respectively. The theory brings out the real significance of the dimension L/T as variability, and significance of inertia in phenomenon with or without variability associating with change of potential, phases or states, the variability being either continuous or intermittent.

The postulates reveal the reasons of the constants occuring in the fundamental laws in modern science, where the reasons have been attributed to the observation being carried out and related to the manifestations occuring along one equipotential spherical surface only in the configuration of the universal spherical wave of energy field. These fundamental constants have been shown to possess all the dimensions E, M, L and T. The associated dimension of gas constant has been derived to be ET^2/L^2 for unit space; temperature is represented as L^2/T^2; Boltzmann's constant K is ET^2/L^2 for unit elementary matter in space; Planck's constant is ET or more appropriately ET/L; Stefan's constant is $E/TL^2 \times (L^2/T^2)^4$. Even π possesses the dimension T/L which is conventionally considered as dimensionless.

Newton's laws of motion, the laws of thermodynamics, the real meaning of absolute zero and entropy have been explained by this theory. The similarity of significance of entropy and probability has been explained. Uncertainty and certainty of positions, the states and phases of energy and matter in the spherical wave configuration have been explained. The limitation of Einstein's equation, $E=MC^2$, and the apparent constancy of observed velocity of light have been explained, and their limited applicability to equipotential context is shown. The present theory explains how it disagrees with the basic assumptions of kinetic theory. The result of Michelson and Morley's experiment is in agreement with the present theory, ether identifying with energy as space itself. Energy is the force in space.

Gravitation of matter entities in energy-space has been explained and the similarity of the relationship of energy and gravitation with that of electricity and magnetism has been elucidated. A correlation between the two manifestations of one into the other has been shown i.e. configuration of energy and gravitation to that of electricity and magnetism and the phenomena of attraction and repulsion have been explained. The phenomena of photo-electric emission, thermo-ionic emission as well as thermo-electricity have been explained.

The conventional ideas of equilibrium have been criticised and static and dynamic states have been

discussed. The significance of Gravitation towards static and dynamic equilibrium states as well as towards higher or lower potentials of energy and matter have been explained. The Law of Mass Action has been interpreted as applying to gravitational reaction establishing a chemical equilibrium. The distribution of energy and matter in the spatial configuration of the spherical wave of energy field has been discussed. The three statistics, viz. Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac, have been discussed. The degeneracy parameter has been identified with dimensional entity ML/ET whose magnitude varied between zero and infinity.

The mechanism of evolution of energy-matter in the light of unversal spherical wave has been explained by numerical expression of the magnitudes of various dimensions. In the configuration of evolution, the static and dynamic states of existence, states of infinity and zero, states with nil or infinite difference in potential have been explained. The significance of transition of evolution from one phase to another, through zero or infinity and through resonance in dynamic or static states has been clarified. The numerical evolution in the radial and equipotential context giving rise to decimal and octet systems has been explained.

In the conventional interpretation of Inverse Square Law in terms of dimensions, the involved dimension as "Square of the distance" is not the distance joining the two but it actually refers to the surface area representing square of the time, which is normal to the direction in space containing the two. Further, it has been explained that in order to have force between them the two cannot be identical.

The conclusions predicted in the Narlikar and Hoyle's theory have been examined in the light of the present postulates; but these, however, are not in agreement with the present theory. The fundamental difference is in the concept of dimensions. Narlikar and Hoyle's theory requires only *two* for creation of an action, whereas, in the present theory no equilibrium action capable of independent existence is possible with less than four dimensions.

The evolution of elementary matter and chemical compounds has been discussed; the mechanisms of exothermic and endothermic processes have been explained.

The mechanism of motion of the planets in orbits in the solar system, and the phenomenon of Ikeya-Seki comet generating gaseous tail which assumes brighter appearance and gets disintegrated while advancing towards Sun, have been explained.

A new approach regarding mode of arrangement of elements in the periodic system has been developed. Suggestions, in the light of the present theory to probe into the mechanism of phenomena like catalytic chemical reaction, the cause of colour exhibition and mechanism of configuration of crystal formation have been put forward.

Present Theory and Sankhyya Science in Ancient India

The postulates of the present theory have been compared with those of *Sankhyya* science in ancient India, and it has been found that postulates of the theory of tetrahedral dimensional universal spherical wave are in agreement in many respects with the ancient *Sankhyya* postulates of *Kapila*. The concepts of fundamental and derived dimensions have been found to be identical in both and the mechanism of evolution in *Sankhyya* science has also been identified as similar to the mode of evolution according to the spherical wave theory. The quantitative limitations of physical perception of a total concept are same in both. The configuration of the tetrahedral dimensional spherical wave also has been shown to be similar in both the cases. The significances of numbers associated with the 22 *Sankhyya sutras* in *Tattasamas* have been examined in the light of the present theory wherefrom it is revealed that the apparently arbitrary numerals associated with the individual sutras were not without meaning. They actually represented the various states and phases of the tetrahedral dimensional spherical wave but found expression in a manner comprehensible within perceptible dimensions permissible and relevant in the remote past.

The postulate in the present theory that any manifestation, capable of existing as an independent equilibrium entity such as the inanimate Universe, must consist of four varying dimensions which are two opposite pairs of two opposites in the configuration of the wave; the various dimensions and their mode of variation representing the configuration in its homogeneous and heterogeneous zones respectively have been found as parallel to those of *Abheda & Bheda* of *Sankhyya* postulates. It has been brought out that the elementary matter and field energy in the heterogeneous field of the spherical wave correspond to *Atmic* consciousness and *Tanmatric Indriya* which are separate. Matter potential and energy potential are similar to *Ahamttatta* of *Tanmatric Indriya* and *Mahattatta* of *Atman* or *Brahma* in nature and magnitudes respectively. Matter as momentum associated with energy forming homogeneous energy field of *two in one* has been shown parallel to the *Dvaita* state of *Indriya Atman* (two in one) and

the fundamental dimension of energy of infinite potential free from matter, space etc. is shown as similar to the absolute dimension as *Parambrahma* or *Parmatma* concept having infinite *Mahattatta*.

The real meanings of Panchabhuta, viz *Kshiti*, *Aap*, *Maryut*, *Tej* and *Byyom*, are actually identified with solid, liquid, gas, space or energy and nothingness or perfect vacuum respectively. The significance of *Prakriti* and *Purusha* in *Sankhyya* in the configurations of the spherical wave are related; *Prakriti* is the evolved equipotential spherical surface and *Purusha* is the configuration of the total concept of *Prakriti* including radial evolution from the centre, which is the position of fundamental dimension. Attention has been drawn to the various *Kundalis*, *Chakras*, *Mudras*, etc. as found in ancient astronomy and astrology and it has been shown that their explanations could be found. Thus, the significance of 9 *Grahas*, 12 *Rashis*, and 28 *Nakhshatras* in ancient Indian astronomy and the various conventional astronomical *Chakras* have been correlated with the tetrahedral evolutionary concept.

It has been shown from the knowledge of the tetrahedral evolutionary configuration with various phases and states, how the ancient Indian scripts, like *Brahmi*, *Maheswari*, *Devanagri*, were evolved and their classification into vowels and consonants in conformity with significance of homogeneous and heterogeneous states in the spherical wave logistically occurs. The significances of the unique symbols like Swastika, OHM as well as the universal symbol of dance embodied in the dancing pose of *Nataraja* incorporating combined configuration of *Prakriti* and *Purusha* has been brought out. Finally, musical sound and mechanism of its evolution and the significance of octets of the musical scales have been explained.

Sulphur—As A Plant Nutrient

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The importance of sulphur as a plant nutrient has been discussed. Sulphur taken up by the plants in the form of sulphate ion lowers the pH of the alkaline or overlimed soils, increases the availability of other plant nutrients and improves the physical condition of the soil. The deficiency of sulphur in the soil and the symptoms due to various reasons have been dealt with. There is a similarity between the sulphur and nitrogen cycles. The characteristics of numerous sulphur-containing materials which may be used as plant nutrients have been discussed.

The importance of sulphur as a plant nutrient has been masked during all these years, because, it is included incidentally in common fertilizer materials like ammonium sulphate, superphosphate, etc. These traditional fertilizers supply the required sulphur even though they have been primarily used for their nitrogen and phosphorus contents.

Within recent years, however, crop failures on account of sulphur deficiency have been reported with increasing frequency from most parts of the world. This has served to focus the attention of the fertilizer industry on means of introducing this important element into the fertilizer products. The main factor for this problem is the trend towards the widespread use of high-analysis sulphur-free fertilizers. Earlier, sulphur used to be applied to the soil as an unrecognized component.

Normal superphosphate has been applied to the soil since long as a phosphatic fertilizer (P_2O_5 18-20%). The sulphur content of the normal superphosphate is about 12 per cent and its requirements by the plants are same as those of phosphorus. Thus, when enough superphosphate is applied to satisfy the phosphorus requirements, the sulphur requirements are also met.

Ammonium sulphate has since long been used widely

TABLE 1—SULPHUR AND PRIMARY NUTRIENT CONTENTS OF CERTAIN FERTILIZERS, %

	Sulphur	*Nitrogen*	*Phosphorus*	*Potassium*
Ammonium Nitrate	—	33.5	—	—
Ammonium Phosphate	—	11	48	—
Ammonium Sulphate	23.7	20.5	—	—
Ammonium Sulphate-Nitrate	15.1	26	—	—
Ammonium Phosphate-Sulphate	15	16	20	—
Ammoniated Superphosphate	11-13	3-7	16-19	—
Calcium Sulphate (Gypsum)	15-18	—	—	—
Diammonium Phosphate	—	21	53	—
Potassium Sulphate	17-18	—	—	48-51
Normal Superphosphate	12-14	—	18-20	—
Conc. Superphosphate	1.4	—	30-50	—
Urea	—	42-46	—	—
Urea-Sulphur	10	40	—	—

as a source of nitrogen (N 20-21 per cent). In addition, it contains nearly 24 per cent sulphur, and the plant requirements of nitrogen are greater than that of sulphur. Thus, when enough ammonium sulphate is used to satisfy the nitrogen requirements, the sulphur requirements are also met.

Potassium sulphate, though used in less amounts, also constitutes an important source of sulphur (approx. 18 per cent).

Function in Plants

One of the earliest recorded responses to the application of a sulphur-containing compound as a plant nutrient occurred in 1768 in Switzerland. Not long after that Benjamin Franklin demonstrated the value of sulphur by applying calcium sulphate to a hillside pasture in Pennsylvania. Since then, it has been established that sulphur is a macro-nutrient along with nitrogen, phosphorus, potassium, calcium and magnesium. It ranks in importance with nitrogen and phosphorus in the formation of plant proteins, some plant hormones, mustard oil glucosides and glutathione. The plant harmones containing sulphur-thiamin and biotin act as plant growth regulators. The mustard oil glucosides impart flavour to the plants, while glutathione is involved in plant respiration. It also influences certain plant processes. Protein synthesis is retarded in sulphur-deficient plants. The presence of sulphur favours the development of nodules and the subsequent nitrogen-fixation by legumes. It is also associated with the formation of chlorophyll. It has also been indicated that sulphur affects carbohydrate metabolism.

Plants take up sulphur almost entirely in the form of inorganic sulphate ion. Elemental sulphur or the sulphides applied to the soil undergo bacterial oxidation to sulphuric acid. The process of conversion of elemental sulphur to sulphate, in the soil, is sometimes referred as sulphofication.

$$\left.\begin{matrix}\text{Sulphur}\\ +\\ \text{Oxygen}\end{matrix}\right\}\xrightarrow[\text{oxidation}]{\text{Bacterial}} SO_2 \longrightarrow SO_3 \longrightarrow H_2SO_4 \longrightarrow \text{Sulphate Ion}$$

In the plants, sulphur combines with nitrogen, hydrogen, carbon, oxygen and other elements to form amino acids, such as methionine and cystine. The various complex proteins are then formed through combinations of these and other amino acids. The amount and the kind of protein that a plant can synthesize and store determine its nutritional value.

TABLE 2—SULPHUR CONTENT OF CROPS

Crop	*Sulphur*, %	*Phosphorus*, %
Corn	8.10	26
Cotton	12.15	20
Wheat	9.12	13
Alfalfa	20.24	21
Clover	15.20	18
Grass	8.10	18
Turnip	29.35	18
Cabbage	19.38	11
Onion	18.20	18

Sulphur and sulphur compounds are generally applied to the soil to perform one or a combination of the following functions: (1) Supply sulphur as a plant nutrient; (2) lower the pH of the naturally alkaline or over-limed soils; (3) increase the availability of other plant nutrients, such as phosphorus, iron and manganese; (4) improve the physical condition of the soil, and (5) reclaim alkali and saline-alkali soils.

Reasons for Sulphur Deficiency

A few of the reasons for the increase of sulphur deficiency may be classified below, if we consider the sources which have been supplying sulphur to the soil hitherto.

Atmospheric Sulphur: Most of the fuels contain sulphur, and when they are burnt sulphur escapes to the atmosphere, whence it is absorbed by water vapour

and comes to the soil with rain. Plants are also capable of absorbing sulphurous gases directly from the atmosphere.

Animal Manure: Manure of animal origin contains a large amount of sulphur compounds, but now-a-days such a manure is losing importance as a fertilizer.

Loss of Soluble Sulphur: Sulphate salts are generally quite soluble and leach from the soil in humid conditions. Sulphur losses are much like nitrogen losses, because conditions favouring decomposition of organic matter cause the accumulation of sulphates and nitrates, which may leach out of the soil if they are not removed by plant absorption. Leaching losses of sulphur, therefore, must be considered in the same manner as those of nitrogen.

Erosion: Erosion also removes sulphur just like other plant nutrients. The losses again may be compared to nitrogen since the profile distribution of sulphur in the humid regions is similar to that of nitrogen and organic matter.

Sulphur Withdrawal: In addition to the above, withdrawal of sulphur from the soil is increasing tremendously through better fertilization and other improved farm practices resulting in better crop yields. But while we have been very careful to supply the plant nutrients like phosphorus, nitrogen, potassium, etc. to the soil, not much importance is being given to sulphur. It is only recently that the fertilizer technologists have come to realize that the soils which are deficient in sulphur give poorer yields and quality of crop, unless sulphur is included as the nutrient. In addition, even the crop response to other primary elements also is limited unless sulphur is added.

Sulphur Deficiency Symptoms

The symptoms of sulphur deficiency of plants are similar to those of nitrogen deficiency. The plants are stunted and become pale green to yellow in colour. Such a chlorosis is severe on the older leaves, but with some plants like citrus, tobacco, cotton, etc., it is even worse on the new growth as well. In contrast to the pattern of nitrogen deficiency, the severely chlorotic leaves of sulphur-deficient plants do not die-back in early stages of deficiency and do not show a characteristic pattern. On some plants like turnips, a marked redness develops in the lower leaves. It starts in the leaf veins and gradually spreads to the interveinal tissues as the deficiency gets worst. However, sulphur deficiency symptoms are not so easily recognised and are frequently confused with similar symptoms of nitrogen deficiency. In addition, the known tests for sulphur in the soil also do not provide an accurate indication of sulphur availability in the soil. As such, these tests may not be a reliable guide for recommending application rates for sulphur.

Legumes use more sulphur than non-legumes, and nodulation in legumes is improved by adding sulphur to sulphur-deficient soils. In many legumes, the sulphur content exceeds that of phosphorus. Some of the earlier data, however, suggest that sulphur serves the same function in legumes as well as in non-legumes and that the nodulation is not directly related to sulphur. A possible explanation is that lack of sulphur reduces the assimilation of nitrogen by a legume and decreases the ratio of carbohydrate to nitrogen in the plant, thereby reducing the activity of symbiotic organisms. Sulphur deficiency on the non-legume crops occur most commonly at high levels of nitrogen fertilization.

Sulphur Cycle

The similarity between the sulphur and nitrogen cycles is most intriguing, though one important difference must not be overlooked. Even in cultivated soils, mineralized sulphur is usually present in rather large amounts—250-1000 lbs/acre under average conditions—but this is not the case with nitrogen. When decomposition of organic matter is considered as a sulphur source for higher plants—and there is no doubt that this is an important source—the similarity between the behaviours of soil nitrogen and soil sulphur becomes very apparent.

When organic matter is decomposed by various micro-organisms, the sulphur-bearing fraction is separated either by assimilation by various micro-organisms or by being further decomposed by bacteria, until the inorganic hydrogen sulphide results. Either in combination with water and oxygen or with oxygen alone, hydrogen sulphide oxidizes quickly into water and elemental sulphur. This is a purely chemical reaction which proceeds rapidly without interaction of bacteria, though various bacteria such as thiotrix, thiobacillus, etc. do assimilate hydrogen sulphide and produce either elemental sulphur or sulphuric acid directy. Whatever process—chemical or bilogical—may be responsible for this conversion under varying circumstances, the elemental sulphur which results is further oxidized into sulphuric acid by autotropic bacteria. Sulphuric acid then combines with various bases to form sulphates.

Reactions

The evolution of inorganic hydrogen sulphide as the end-product of the decomposition of organic matter, eompares with the production of inorganic ammonia in the nitrogen cycle. Just as ammonia is oxidized by

bacteria into nitric acid, which combines with bases to form nitrates, so is hydrogen sulphide oxidized to sulphuric acid from which sulphates are formed. That part of the hydrogen sulphide, which the micro-organisms assimilate for the synthesis of proteins, has to be decomposed once more when the bacteria die, before the sulphur becomes available again, in much the same manner as with ammonia. The similarity goes even further. Just as nitrates may be reduced under anaerobic conditions (when oxygen is lacking) to elemental nitrogen, so sulphides may be used by bacteria as a source of oxygen, especially in soils which are water-logged.

Thus the eternal round of the sulphur cycle includes oxidation and reduction, synthesis into proteins, and the decomposition of proteins which contain sulphur. The soil conditions which favour a smooth progression of these processes are very much the same as those which favour ammonification and nitrification.

Sources of Sulphur

There are numerous materials available which may be used as a source of sulphur as plant nutrient. Some of these are standard fertilizer material, ordinarily applied for their contents of a primary plant nutrient, while others are used solely for their sulphur content. The following are some of the sources.

Sulphuric Acid: Sulphuric acid is added to the soil to check soil alkalinity and supply sulphur. Earlier, its application used to be done by metering it into irrigation waters. More recently developments indicate that direct application or injections into the soil may find wide application.

Ammonium Sulphate: It is widely used since long as a source of nitrogen to the soil but is losing ground more recently. In the soil it is oxidized to give sulphuric and nitric acids, whence the sulphate and nitrate ions become available to the soil.

Ammonium sulphate → Sulphuric acid → Sulphate ion
Ammonium sulphate → Nitric acid → Nitrate ion

Ammonium Nitrate-Sulphate: The double sait is made by neutralising sulphuric and nitric acids with ammonia, but the sulphur contents are very low (5 per cent). It contains 76 per cent ammonium nitrate, 21 per cent ammonium sulphate and 3 per cent conditioners.

Calcium Sulphate: Gypsum and anhydrite have long been used for the fertilization of soil. Gypsum is an important constituent of superphosphate.

Potassium Sulphate: It has been used primarily as a source of potassium and also contains about 18 per cent sulphur.

Aluminium & Iron Sulphate: These metallic sulphates are added to acidify the soil. They are hydrolysed by the moist soil to give sulphuric acid and then the sulphate.

Metal Sulphate + Water → Hydroxide + Sulphuric acid → Sulphate ion

Sulphurized Superphosphate: In certain countries, viz. Australia and New Zealand, superphosphate is fortified with elemental sulphur, thus getting a product having 18-36 per cent sulphur and 64-82 per cent superphosphate. The product contains homogeneously distributed finely divided sulphur.

Enriched Superphosphate: The phosphate rock can be acidulated by a mixture of phosphoric and sulphuric acids. Thus, some sulphur is introduced.

Ammoniation & Granulation: Whenever solid fertilizers are processed through an ammoniation and/or granulation unit, sulphur may be introduced by adding sulphuric acid followed by neutralization with ammonia or an ammonia-containing solution, thus forming ammonium sulphate.

Urea-Sulphur: Urea-sulphur is made by fusing urea and elemental sulphur, followed by prilling. The product generally contains 40 per cent nitrogen and 10 per cent sulphur, although the ratio is adjustable. On application to the soil, urea gets dissolved in water while sulphur gets deposited and is converted into a sulphate by soil bacteria.

Urea-Sulphate Complexes: Urea forms complexes with several sulphates. Thus, it reacts with sulphuric acid to form the complexes containing one and two molecules of urea per molecule of the acid. In gypsum, the water of crystallization is replaced by urea to give $CaSO_4.4CO(NH_2)_2$. Also with magnesium sulphate, complexes containing one, five and six molecules of the salt per molecule of urea have been prepared.

Elemental Sulphur: The addition of elemental sulphur to a soild mixed fertilizer is the most obvious way of getting most of the sulphur with the least weight increase and consequently the least reduction in grade of the other plant food elements. Unfortunately, the best method of introducing elemental sulphur has yet to be determined.

The rate of conversion of the elemental sulphur into sulphate in the form available to plant depends upon the particle size of the sulphur. It has generally been

indicated that the particle sizes of 80-100 mesh (B.S.S.) below are most effective.

Another difficulty with the use of elemental sulphur is because of segregation and fire hazard problems. In some cases, it has been observed that steam or water-fog is helpful in minimizing dusting and development of static electric charge.

Investigations are, however, still going on to determine more suitable methods of adding elemental sulphur to fertilizers. Finely ground sulphur has been incorporated with diammonium phosphate, triple superphosphate and nitrophosphates using only water as a granulating media. Other possibility is that of adding molten sulphur to form thin converging films on fertilizer granules. The above processes are being studied by the Tennessee Valley Authority while the U.S. Department of Agriculture are conducting experiments on the addition of ground elemental sulphur of different particle size ranges into superphosphate in various ways. In one series, sulphur was added before acidulation of the ground phosphate rock. In another, it was added to phosphoric acid and in the third, it was mixed with the acidulated slurry, followed by subsequent granulation. Agronomical studies are still going on. Methods of adding sulphur to diammonium phosphate are also being investigated. Attempts are also being made to prepare a granular form of sulphur alone, which could be suitable for use as such by bulk blending with other fertilizers.

Ammonia-Sulphur: The use of ammonia-sulphur solution is being studied with a view to simultaneous and uniform application of both nitrogen and sulphur. The solubility of sulphur in ammonia is inversely proportional to temperature. Between 32° and 120°F, it ranges from 32 to 15 per cent. When this solution is applied to the soil, ammonia vaporizes and subsequently reacts with the soil constituents, leaving fine deposits of elemental sulphur. This sulphur is then converted rapidly by the soil bacteria to sulphate in the form available to plant. Studies are, however, still going on at the T.V.A. on the various aspects of the problem.

Micro-nutrients: Most common micro-nutrients are metal sulphates which can be added to liquid fertilizers primarily for their micro-nutrient content. In all, they add a significant amount of sulphur to the fertilizer solution.

Sulphur Dioxide: Experiments at the Washington State University have shown that liquid sulphur dioxide may be injected directly into the soil to serve as source of sulphur. A rate of application of 64 lb/acre of sulphur equivalent is sufficient for most crops and no adverse effects have been noted under these conditions.

Polysulphides: Ammonium polysulphide is a chemical product of hydrogen sulphide with ammonia. In its usual form, it is a red liquid containing about 20 per cent nitrogen and 40-45 per cent sulphur. However, samples of different analysis can also be prepared. It can be applied directly to the soil as well as through irrigation waters or with ammonia- and nitrogen-containing solutions. In acid medium it, however, decomposes.

Calcium polysulphide has also been used for direct application to the soil. When applied in combination with ammonium polysulphide, there is a partial decomposition with the release of dispersed elemental sulphur which is subsequently oxidized to sulphuric acid.

Ammonium Thiosulphate: This is another sulphur-containing material which is gaining popularity in recent times. It can also be applied in irrigation waters or with many fertilizer solutions like aqua ammonia, nitrogen solutions containing ammonium nitrate, urea solutions and most nitrogen, nitrophosphate or complete fertilizer solutions. It cannot, however, be mixed with anhydrous ammonia or acid solutions such as phosphoric acid because of decomposition of thiosulphates.

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In the Indian Context

Raw Materials for Fertilizers—Their Processing and Significance in Future Fertilizer Production

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Self-sufficiency is the motto of every developing country. Keeping in line with this, this paper emphasises that the sole criteria in drawing out schemes for fertilizer production should be based on the country's own resources and capabilities. The relative economics of various process technologies based on different raw materials have been discussed and the best utilisation of indigenous feedstocks has been pointed out. It has been shown that coal and its subsidiary products, which are available in abundance, could offer an economic alternative to petroleum naphtha which will remain an imported item for some time to come.

A critical estimate of massive size plants, based on centrifugal and reciprocating compressors, has been made. In the context of the present-day development of the country and taking into account factors like planned intensity of fertilizer application, problems involved in the distribution of finished products, limitations in transportation, developed facilities for fabrication of equipment and machinery, resources within for repairs and maintenance, saving in foreign exchange by utilizing machinery capacity which is being indigenously developed, etc., uncritical acceptance of the view that centrifugal compressor based massive plant is the only technology to be adopted, is not in the interest of the country and is definitely not in the line with the long term planning of fertilizer industry in a developing country like India.

On phosphates, the paper points out that the emphasis on production of a single water soluble phosphatic fertilizer like ammonium phosphate is absolutely not valid in the present-day context. In a country with practically no resources of immediately available sulphur or sulphur substitutes, the choice of sophisticated products is harmful and must be given up, particularly in view of the world sulphur shortage and the difficult foreign exchange position. Citrate-soluble phosphates, including dominantly citrate-soluble nitrophosphates, should be good enough to meet the immediate needs of the country at least for years to come. While deciding on the pattern of phosphatic production, minor objection as to the efficacy of citrate-soluble phosphatics and nitrate nitrogen must not be unduly over-emphasized as that may lead to wrong planning.

Intensive cultivation, which alone can secure agricultural self-sufficiency for India, would require concomitantly intensive fertilizer application. The projected requirements of fertilizers during the Fourth and subsequent plans are enormous which cannot conceivably be fulfilled by imports. Nothing short of an all-out effort, based completely on self-reliance both for putting in the necessary manufacturing capacity and operating it, can hold out hopes for realising the minimum targets set. In drawing up the manufacturing schemes, the questions of raw materials and the processing technology to be adopted become the major factors, and the sole criteria in selecting either must be based on the country's own resources and capabilities with reliance on sustained production independent of any possible shifts in international situation. This paper attempts a brief review of all these aspects in respect of the fertilizer industry in the prevailing context in this country.

Nitrogenous Fertilizers

Nitrogen from air and a cheap source of hydrogen are the basic raw materials for the production of ammonia, the primary intermediate for nitrogenous fertilizers. Water and the various types of carbonaceous feedstocks are the principal sources of hydrogen. Hydrogen can be obtained directly from water only by electro-chemical methods. Further use of electrochemical methods beyond the present installations is, however, ruled out, because of adverse economics and the overwhelming

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demands on electric power for other uses as against restricted supplies thereof.

Sources of Hydrogen

The sources of hydrocarbons, the potential feedstock for hydrogen, range from natural gas, through liquids like crude oil and its distillate fractions to solids viz. coal, lignite, etc. Gases obtained from manufacturing processes, such as refinery off-gases, coke oven gas, etc. can also be effectively tapped as sources of hydrogen. Here the availability position of each of these in this country has been discussed briefly.

Natural Gas: Its sources exist mainly in Assam. Recently these have also been located in Gujarat. The Assam deposits are by far the biggest now. The gases occur partly with petroleum crude and partly as non-associated gas. A plant under construction at Namrup for an output of 45,000 tonnes of nitrogen as urea and ammonium sulphate is based on this gas. Potentially the gas which will be available during the Fourth Plan period can support a fixed nitrogen production equivalent to 200,000 te annually if completely earmarked for fertilizer manufacture. However, in establishing such production facilities a proper assessment has to be made regarding the intensity of fertilizer application in the region during the coming years and the problems involved in the transport and distribution of the product. While schemes for proper utilization of Assam's natural gas resources are being formulated and put through where sanctioned, a good deal of associated gas from oil wells is likely to be flared off for want of any other useful outlet. Since this is a premium feedstock for fertiliser production, in the overall interests of the country expedients like pumping the released gas back into the crude reservoirs, etc., which could conserve this valued raw material for use in future, should be seriously considered.

The available output of natural gas from the Gujarat deposits has been already earmarked to various industries. Though a part of it would be used for fertilizer production at Baroda, by and large, it is to be used for power generation as fuel and feedstock for other industries. As a matter of fact the allocation for the Baroda unit is barely adequate to support about half of the proposed capacity of 90,000 te N/yr and recourse to naphtha has to be taken to cover the gap. Intensive exploration in other areas in Gujarat and elsewhere may bring more deposits of gas to provide additional feedstock. It would be in the overall interests of the country to accord high priority in allocation of these fresh resources as feedstock solely required for fertilizer capacity.

Light Distillates: Light distillates from petroleum refinery operations provide another raw material for hydrogen production.

The refinery off-gases, especially, are a good source material. They are amenable to economic processing; in some cases, they may even contain some free hydrogen. Usually this gas fraction is used as a fuel in the refinery after removing certain portions from it, which may either have a market as LPG or provide the primary feedstock for petro-chemicals. However, refineries should be induced to meet their internal fuel needs from heavier distillate feedstocks with limited market value. The valuable gas fraction can then be released for fertilizer production. The FCI Unit at Trombay is already processing some refinery off-gases to fix about 40,000 tonnes of nitrogen annually and a similar scheme for Barauni appears to be in the offing. In all other refineries in future, which have assured supply of indigenous crude, similar schemes of off-gas utilization should be given consideration.

Another light distillate which is being increasingly used as a feedstock for hydrogen is the *light petroleum naphtha*. The promotion of naphtha as a fertilizer feedstock in this country started with a situation where this particular fraction was left in our refinery programmes as a considerable surplus for disposal. This was due to the fact that the country's refining programmes were primarily drawn up to meet demands for the middle distillates, such as kerosene, diesel and furnace oils. Surplus naphtha was then offered at subsidized prices as feedstock for fertilizer production and was even suggested as a supplementary fuel for injection into blast furnaces, although with only a few additives, it commands a much higher price as a fuel for internal combustion engines. Meanwhile, certain adaptations and improvements in catalytic steam reformation process removed the restrictions on its applicability to gaseous hydrocarbon feedstock alone and enabled naphtha to be processed to synthesis gas to some extent more economically than by the established partial oxidation techniques. In the USA, plans and engineering designs were also evolved based on the concept of massive single trains of equipment centering around the use of centrifugal compressors. With natural gas or naphtha as feedstock it was claimed that the much publicized 'New Technology' could bring about drastic reductions in capital and operating costs of ammonia production. Indeed the eulogies on massive plants and merits of naphtha as a feedstock for ammonia production have been carried to such an extent in this country

that an impression has been created that any scheme other than the naphtha-based massive fertilizer plants is not worthy of consideration in future. Serious implications of this line of reasoning naturally require very careful and objective appraisal. Plant capacities at any location have to be chosen in the context of the intensity of fertilizer application in the region taking into account the problems involved in the transportation and distribution of the products. The impression that has been created in favour of the massive plants irrespective of the location and the size of the market is misleading since the aim of economies in production is to achieve the lowest cost of fertilizer as delivered to the farmer.

The serious implications of consigning the whole of the future fertilizer programme to naphtha as feedstock has also to be carefully assessed in planning the future fertilizer programme in the country especially at the present juncture. Petroleum naphtha could only in a very limited sense be classed as an indigenous commodity. It is, by and large, an indirectly imported feedstock, since as much as 80 per cent of the crude oil currently used by the refineries are imported. Even at the end of the Fourth plan 60 per cent or more of the crude will be imported. The availability and prices of crude may therefore be subjected to international trading pressures, and, in cases of hostilities, disturbances to trade channels on the high seas, etc. Under these circumstances it runs counter to the concept of 'self-reliance' if we were to commit a major portion of our fertilizer programme to a source material subject to these vagaries.

While naphtha to the extent available from indigenous crudes can be used for fertilizer production, it would indeed be totally indiscreet to make such a vital sector of our economy as food production dependent on naphtha, based on imported crude. Secondly naphtha can be allocated to fertilizer industry only after fully meeting the needs of civilian transport, defence requirements, etc. If perchance crude supplies were to dwindle, a clear idea of priorities which will be given in allocation of available supplies, has to be worked out in advance. The surplus availability figure itself is a quantum which is still to be settled definitely. There is an even chance of its being reduced below the present allocation or even disappearing altogether if the targets for refinery capacity—which has already once been toned down from 28 to 22 million te crude throughput/year—is further revised downwards.

Straight-run naphtha is the preferred feedstock for catalytic steam reformation process. But this category of naphtha has to meet competing demands from the petrochemicals side as well. Petrochemicals normally fetch a much higher value than fertilizers. Petrochemicals industry therefore can afford to pay higher prices for naphtha than the subsidized rates extended to fertilizers. Given a free choice, perhaps the refineries would much rather dispose of naphtha through more profitable channels like petrochemicals than for fertilizer manufacture at subsidised rates. It requires careful consideration from overall point of view whether available surplus naphtha would be better utilized in petrochemicals field or for fertilizer production especially since compared with its intrinsic value as feedstock (without a subsidy) it can offer only marginal cost advantages over other alternate feedstock which in addition have the virtue of being freely available within this country. In case of hostilities one can very well do without some of the luxury items coming under petrochemicals but not without fertilizers vital on the food front.

Heavier Distillates: Heavier petroleum feedstock, like fuel oil, can be successfully gasified and processed to synthesis gas mixture using the non-catalytic high pressure partial oxidation process—technique installed in Trombay and being adopted at Gorakhpur units of FCI Ltd. Since the availability of this category of feedstock for fertilizer production at economic prices has not been indicated, their consideration in the present context is precluded.

Coal & Lignite

The resources of coal and its subsidiary product within this country are abundant. Indeed this offers the ideal source of feedstock for fertilizers from the point of view of assured supply under all circumstances and availability at a wide variety of potential production centres.

Coke Oven Gas: It is obtained as a by-product in coke-making operation. The gas contains nearly 50 to 55 per cent free hydrogen, which contribute roughly to just over a third of its heating value, which in most cases is wasted away as a fuel. It is estimated that roughly for every 15 te coal carbonized in coke ovens, sufficient free hydrogen is liberated to fix 1 te N.

Only at Rourkela this scheme has been adopted to use the hydrogen, but even there, a shortfall on the availability of the gas has turned to the detriment of fertilizer production because a much higher priority is given for using the gas as fuel in steel manufacture. But in view of the importance now attached to fertilizer and food production, this source of by-product hydrogen should not be allowed to be wasted as fuel. It should be possible to arrive at an arrangement whereby ancillary

fertilizer units be set up side by side with all steel-making plants for using all coke oven gas, because as a feedstock for ammonia production it is second to none. It should be possible to rearrange fuel consumption patterns within the steelworks to substitute the use of coke oven gas with either lean fuel gas from undersize coke or, if presence of illuminants is considered necessary, by producer gas from non-caking coals. Coke oven gas is amenable to processing by catalytic steam reformation perhaps even more easily than natural gas or naphtha. The use of the entire coke oven gas produced from the existing steelworks for fertilizer production can generate a capacity of 800,000 te N/yr. to be furnished as urea, calcium ammonium nitrate or nitrophosphate, according to the requirements and convenience in particular areas. Schemes on these lines are possible in all steelworks and should be considered for inclusion, for instance, in the Bhilai or Durgapur Steelworks extensions or for incorporation in the Bokaro project.

As already mentioned, coal and lignite constitute a vast indigenous source of raw material of fertilizer industry. But Sindri and Neyveli are the only two projects now based on such solid feedstocks. There has been a recent tendency to relegate these feedstocks for secondary consideration because they require a higher quantum of investment, employ outmoded processes and bring about a higher production cost. It may be true that the costs for conversion of gaseous and liquid hydrocarbons (excluding feedstock prices) to synthesis gas show an advantage over those of processing solid fuels to the same end-product; amenability of the former to pressure processing, absence of associated dross like ash, favourable effect of a lower carbon to hydrogen ratio on total quantum of processing, etc., as compared to coal, are the factors responsible for their preference. It would, however, be wrong and misleading to postulate that under all circumstances coal and its subsidiary products can never produce fertilizers at a cost competitive to those from, say, naphtha or natural gas.

Comparison between Coal and Naphtha

The very basis of comparison is too often inequitable. For example, the price of naphtha is an artificially pegged one. It has been fixed at Rs. 85.00 per tonne. This has no relation to the cost of production of naphtha or total processing costs in the refinery or natural free market. It has been estimated that for a refinery capacity of 1 to 2×10^6 te/yr of crude oil based on Indian crude, the cost of production of naphtha may be around Rs. 130/te. This price compares with about Rs. 108 to Rs. 115/te of naphtha and light distillate in European countries. While comparing the advantages of the two processes, the intrinsic worth of the raw materials should be taken to bring the data on the same level. On the one hand, naphtha is given the advantage of a subsidized price structure which bears no relationship with cost of production or its free market value. On the other, coal is put at an added disadvantage by adopting a price structure which makes no allowance for its caking or non-caking characteristics nor sets a direct relationship between prices and calorific value. It may be mentioned that processing of primary gas from coal-based operations can as easily be adapted to the concept of massive single stream operation as with naphtha. Tables 1 and 2 show an equitable comparative evaluation between identical capacity coal-based and naphtha-based plants laid out on these lines. The study showed that the processing cost of ammonia from coal could work out cheaper than that from naphtha if the inequities in pricing of these feedstocks are properly compensated and the fixed charges on investment are excluded. The figures derived would represent conditions when the installed plant has been completely paid back. Indeed if the retention prices per te N after allowing a 10 per cent return on capital in the case of steam driven centrifugal compressor based naphtha plant be taken as the standard for comparison, and the differential between the annual operating costs and the sales turnover is used for paying back the investment, it should be possible to amortize a coal-based plant within 5 to 6 years if the corresponding naphtha-consuming plant based on steam-driven centrifugal compressors is assumed to have a payback period of 5 years. Thereafter coal-based operation would indeed represent a cost advantage of 12.5 to 19.5 per cent over naphtha-based operation. Indeed when we set out to make an economic comparison between the two raw materials, the operating costs after amortization should represent the intrinsic relative advantages which the conventionally worked out production costs fail to do. One cannot forget that the concept of amortization allowance, etc., which contribute to fixed costs in conventional production cost calculations, is a purely arbitrary one, regulated on the basis of fiscal measures announced from time to time. They hardly represent the intrinsic residual worth of a piece of investment. Thus, if a really balanced and objective economic evaluation be made with price of naphtha allocated its true value, it can be seen that cost of production of NH_3 (including fixed cost) for coal-based plant using steam-driven centrifugal compressors becomes cheaper than a corresponding naphtha unit. Here

TABLE 1—COMPARATIVE INVESTMENT COST: 600 TE/DAY AMMONIA PLANT

(Naptha based—Centrifugal Case—base index 100)

Sl. No.	Items	*Composite Machines—Synthesis Gas Compressor & Recirculator—Reciprocating Motor Driven. Others—Centrifugal Steam Driven.*				*Centrifugal Machines—All Steam Driven*			
		Coal	*Naphtha*	*C.O.G.*	*Natural gas*	*Coal*	*Naphtha*	*C.O.G.*	*Natural gas*
1.	*Equipment Cost*	160.00	99.40	94.50	98.00	161.00	100.00	94.60	94.50
	Total:	154.00	98.90	93.00	92.00	164.00	100.00	94.40	92.90
2.	*Erected Plant Cost*	134.50	99.50	76.60	76.80	134.20	100.00	78.50	77.40
3.	*Working Capital*								

TABLE 2—PAYBACK PERIOD

1. Processing Cost (excluding depreciation and interest charges)	81.30	93.20	75.60	55.50	78.50	100.00	75.50	54.70
2. Cost of Production (including all fixed charges)	100.80	94.60	79.60	63.70	93.60	100.00	79,70	63.50
3. Cost with 10% return on capital	160.00	95.40	81.00	66.60	101.00	100.00	81.50	65.40
4. Payback Period, Yr	5.27	4.27	2.97	2.26	5.14	5.00	3.34	2.26

the plea is not that the naphtha price should be increased but that similar indirect subsidy should be given to coal used in the fertilizer industry. Indeed as the only dependable, firmly indigenous and assured source of raw material for future fertilizer programmes in this country, coal should be given a premium over naphtha. It is a matter for wonder as to which interests are being ultimately served by loading our own abundant resources with levies and imposts, and subsidising prices and bringing into favourable light a commodity for which we have to depend indirectly on external sources due to limitations in availability of naphtha based on indigenous crudes.

Processing Technologies

The processing technology of industrial hydrogen has attracted a good deal of attention recently. Laudatory accounts of what are considered to be giant strides made abroad in the fertilizer field have been presented along with claims that all plants in operation in this country now may be considered obsolete. In a matter like this, however, one has to be on one's guard not to be swept off one's feet by highly coloured versions of the virtues of certain techniques which are often put forward as high pressure sales points. While the new techniques have their good points, one has also to consider under what circumstances these are really advantageous in our context.

Any serious student of technology would concede that every technique has its own range of applicability within which alone it may claim an advantage over its alternatives. The 'New Technology' has its restrictions. In its pristine form it is receptive only to a narrow range of feedstock—predominantly gaseous hydrocarbons and to straight-run light petroleum fractions with rigid limits on certain constituents like sulphur, carbon to hydrogen ratio, etc. The massive single units with a high daily output are well adapted to conditions where intensive and assured fertilizer off-take can be foreseen. If the units are to serve widely dispersed distribution zones they can create formidable storage and transport problems. In examining the applicability of these techniques to our context we have to examine the implications with reference to the situation in the country. For instance, allowance has to be made for the level of maintenance skills and facilities within the country. Where we are anxious to save on foreign exchange outflow either for capital items or on recurring operating account, equipment design and process selection has to be carefully weighed from this angle. Above all, an uncritical acceptance of sales talk on techniques and products developed abroad should be carefully avoided.

One particular illustration may be given. It has been claimed that use of centrifugal compressors in ammonia synthesis brings about a spectacular reduction in power consumption. In actual practice, however,

TABLE 3—RAW MATERIAL AND UTILITY COSTS

(assumed for calculations)

Items	*Unit*	*Unit Cost Rs.*
A. RAW MATERIAL		
1. *Naphtha or other Petroleum fraction used as:*		
(a) Process feedstock	Te	130.00
(b) Fuel for Reformer/steam generation	Te	177.00
2. Coal (10,200 Btu/lb.)	Te	25.00
3. Coke Oven Gas	10^6 Kcal	10.00
4. Natural Gas	Nm^3	0.0535
B. UTILITIES		
1. *Steam*		
(a) Fuel oil	Te	19.00
(b) Natural Gas	Te	9.00
(c) Coal (10,200 Btu/lb.)	Te	9.00
2. Power	1000 KWH	50.00
3. Process Water	M^3	0.15
4. B. F. Water	M^3	0.50
C. NO. OF STREAMS	One	
D. CAPACITY	600 Te/day	
E. FOR STEAM GENERATION, (coal is used for coal and coke oven gas based plants, fuel oil for naphtha based plants and natural gas for natural gas based plants).		
F. CENTRIFUGAL COMPRESSORS	One compressor. No standby.	
RECIPROCATING COMPRESSORS	Two 50% compressors. No standby.	
G. EQUITY CAPITAL	50% of total capital.	

for identical compression duties, a centrifugal compressor would consume approximately 10 per cent more energy in case of a 600 te/day ammonia plant and 5 per cent more in case of a 1000 te/day ammonia plant than a corresponding set of reciprocating machines. In some of the newer plants, however, drives are arranged from steam turbines in place of electric motors so that the absolute figures in power consumption are kept down and shown off as spectacularly low. Lower synthesis pressures are employed to enable an all-centrifugal application. Actually from process point of view this is a departure from optimum conditions either on investment or operating requirements on the synthesis loop; the energy savings made on compression duties on synthesis gas are nearly evenly balanced by increased requirements for recirculation of gas and refrigeration to separate out ammonia product. A 10 per cent saving in capital costs is claimed on substitution of centrifugal machines for reciprocating ones. The assumption is that no standbys will be provided for centrifugal compressors. As a matter of fact if standbys on reciprocating machines are also removed, the installed costs on the two types of machines show an advantage on reciprocating machines. Higher on-stream times are claimed for centrifugals. But this is still to be proven in practice, over a sufficient number of years. Sometimes for massive single stream units on-stream ratings of as low as 82 per cent are given as against 95 per cent for a multi-stream unit with adequate standby equipment.

This is indeed an important consideration for us in this country as to date none of the plants which attempted operation whether on single or multiple stream, without standbys, has had a smooth time in starting up or registered full-rated production consistently thereafter. A factor which contributed largely to this is the difficulty too often faced in securing and maintaining adequate stocks of imported maintenance components. In short, the point to be emphasized is that in taking vital decisions with far-fetched consequences on the country's economy, at this stage, proven reliability in processing technique and full provision for assured quantitative production should carry a much higher weightage than marginal economic advantages. Absolute dependence on the latest technology will mean increased dependence on import of equipment and machinery and that too from rather very restricted sources. In this light, adoption of established and proven technology with promise of a higher draw-off from indigenous resources should be the better choice for us in the situation as it is to-day.

Before I close on this subject, a word on the so-called 'obsolete' technology in our existing fertilizer units seems to be in order. It may be pointed out that the 'newest' naphtha-based units follow substantially same sequence of process steps as in FCI's natural gas processing unit at Namrup. The existing partial oxidation units using naphtha—at Trombay and Gorakhpur units of FCI—are even now versatile enough to handle any naphtha and if it comes to a pinch even fuel oil or heavier fractions. It may be mentioned here that due to the tight position of availability of surplus naphtha, it has even been considered whether the versatile units at Gorakhpur or Trombay could process off-specification naphtha or even switch over to fuel oil to accommodate the needs of naphtha for plants based on 'New Technology'.

Phosphatic Fertilizers

Turning now to phosphatic fertilizers, the primary raw material, viz. rock phosphate, is at present imported. Some occurrences of phosphatic rock have been re-

ported in some parts of the country but none of a size to meet any appreciable part of our needs. Some interest in the possibility of off-shore submarine deposits of phosphate mud and rocks was also stimulated by the oceanographic survey ships which went round the Indian ocean. Survey and investigation to locate and prove rock phosphate deposits should therefore be given the highest priority.

The requirement of rock phosphate for target production of 1 million tonne P_2O_5 set for the end of the Fourth Plan, would at the present day price levels, entail a foreign exchange expenditure of over Rs. 25 crores. While barter deals with traditional Middle East countries for rock phosphate have been satisfactory for very limited amounts covered by present requirements, the matter of permanent long-term arrangements for supply of phosphate rock for future will have to be taken up in earnest for which provision shall have to be made on a stable basis.

The phosphatic fertilizer manufactured in this country to date are superphosphate and ammonium phosphate only. These forms, however, require of sulphur—0.72 to 0.76 te/te P_2O_5 for super and 0.965 to 0.995 te/te of P_2O_5 for Amm. Phos.—besides phosphate rock. If all the phosphates covered by Fourth Plan target were to be supplied in these forms alone and the requisite sulphur imported, an additional foreign exchange bill of Rs. 20 crores/year will have to be provided for. The sulphur market, moreover, is closely regulated by a group of producers and is subjected to periodical gluts and lean periods with prices fluctuating in sympathy. Just at present the market is hardening and prices spiralling up. It would therefore be hazardous to plan phosphatics production on the basis of imported sulphur. Fortunately, agronomic trials have revealed that with the present soil nutrient status and rates of off-take in general no significant difference in response is noticeable by application of either water-soluble or citrate-soluble phosphatics. The relative merits of these forms of phosphatics have been in the past a subject of considerable controversy not only in this country but abroad too. Even in USA, where ammonium phosphates and superphosphates are the most widely marketed forms, at a recent agronomical conference at the Tennessee Valley Authority the problem was subjectively analysed, and several specialists concluded that in most cases citrate-solution phosphates would adequately satisfy crop needs and that even where water solubility is considered desirable, more than 40 per cent is unnecessary. Another significant feature of the behaviour of phosphatics when applied nutrient remains in the soil to build up a nutrient reserve which the plants can avail of in the long run; unlike nitrogen, the applied phosphatics are not lost easily by decomposition or leaching besides absorption by plants.

Methods are available whereby phosphatics in an acceptable form can be prepared from rock phosphate without using sulphur. For instance, using nitric acid for solubilisation of rock, a multi-nutrient complex can be furnished. The Trombay Unit of FCI is equipped to manufacture this product. From the point of view of restricting imports and maximizing self-reliance, this type of product should be manufactured, wherever possible. Water solubility to the extent desirable can be introduced into the product by incorporating sulphate radical from indigenous resources in the course of its preparation. There may still be some areas and certain crops in the country for which water-soluble phosphatics may be considered as the comparatively more effective ones for use.

To serve such areas, phosphatics production should be developed wherever sulphur-bearing gases are available economically as by-products of other manufacturing operations. Khetri, Udaipur, Ghatsila are some of the locations at which schemes have been suggested. FACT's plant at Alwaye is already attempting a similar scheme in conjunction with a zinc smelter being put up nearby. These sources of sulphur can be supplemented by processing sulphur-bearing ores like pyrites, of which deposits have been located at Amjore (Bihar) and in Rajasthan. Such schemes should, however, be judiciously drawn upon for production of phosphatics. Wherever possible, recovery and recycle of sulphate radical for more solubilization of phosphates should be attempted. The economics of recovering sulphur from gypsum, either the naturally occuring variety or one recovered as a by-product in rock phosphate solubilization, should be studied.

Indeed this field offers a great challenge to the indigenous technology. The native ingenuity can rise to the occasion and provide the ways and means of husbanding our available resources and facilities provided fair opportunities are given, and confidence reposed and, above all, the objectives of self-help and self-reliance kept in view. The quantitative outputs based on maximum 'self-reliance' should be the end and aim of our efforts in this field. Controversies and quibblings over relative efficacies of types of fertilizers manufactured have no place in the present situation. Indeed many of the arguments, being advanced off and on, on the efficacy or otherwise of

phosphatic forms applied to soil, are not anywhere near being conclusively substantiated by field experiments.

View-points have also been often put forward that nitrate-nitrogen is comparatively less effective as a plant nutrient as it is liable to be easily leached and is subject to denitrification under reducing conditions prevalent under water-logged conditions. Such views expressed to rule out manufacture of nitrophosphates have not been borne out by experiments and trials. All the recent trials carried out under better farm management conditions in the different experimental stations in our country[1] indicate no significant difference in the efficacy of nitrate-nitrogen as compared to ammoniacal nitrogen.

Theories and opinions have to give way to actual field observations, especially where they have subtle overtones ultimately leading up to the inevitability of tying up this country to purchase of commodities like sulphur or phosphoric acid, which in the situation today one cannot under any circumstances afford. In any case if one cannot have the best, one should be satisfied with the second best. In the present context no objective is more sacred, and no sacrifice of advantages too great, than the task of putting this country in a position economically and politically immune to unhealthy pressures from whatever directions they may come.

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CORRIGENDUM

Printing Error on p. 147 in the paper "Kinetics of Dry Box Purification" by V. P. Singh and U. R. Warhadpande, Vol 2, No. 3, July - September 1965.

Equations (5), (9) and the last equation on this page should be read as follows:

$$\frac{-\log S_1}{-\log S_2} = \left(\frac{V_2}{V_1}\right)^{0.6} \qquad \ldots.(5)$$

$$\frac{-\ln S_1}{-\ln S_2} = \frac{(kga)_1}{(kga)_2}\,\frac{V_2}{V_1} \qquad \ldots.(9)$$

$$\frac{-\ln S_1}{-\ln S_2} = \left(\frac{V_2}{V_1}\right)^{0.6} \qquad \ldots.\text{last equation}$$

On Reduction of Formation of Unavailable Phosphate in Mixtures of Superphosphate and Calcium Ammonium Nitrate

By

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The formation of water-insoluble and citrate-insoluble phosphate, when superphosphate is mixed with calcium ammonium nitrate, has been reduced considerably by incorporating suitable proportions of magnesium sulphate in the mixture.

The major proportion of N-P fertilizer mixtures, now being manufactured in India[1], is obtained by bulk blending of ammonium sulphate and single superphosphate in different ratios. Calcium ammonium nitrate has not so far been used in the preparation of fertilizer mixtures although considerable quantities of this material are being produced in factories at Nangal and Rourkela. Kanwar[2] et al have examined the feasibility of preparing N-P fertilizers by mixing calcium ammonium nitrate with superphosphate. They found that water-soluble phosphate in the mixture showed a very rapid conversion to a water-insoluble, but citrate-soluble, form and the latter further changed to a considerable extent into a citrate-insoluble form in the course of two months.

The present investigation was undertaken to find out methods by which the formation of water and citrate-insoluble phosphate in the superphosphate-calcium ammonium nitrate mixture could be minimized. Substances like magnesium sulphate have been used[3] to prevent the formation of citrate-insoluble phosphate from citrate-soluble dicalcium phosphate during the manufacture of nitrophosphate by the carbonitric process. In the present study, addition of magnesium sulphate to superphosphate-calcium ammonium nitrate was first tried to see whether this is effective.

The superphosphate used contained: Total P_2O_5 20.30; Water-soluble P_2O_5 17.21; Citrate-insoluble P_2O_5 0.42 per cent, while the calcium ammonium nitrate contained: Ammoniacal N 10.26; Nitrate N 10.43 per cent. The superphosphate and calcium ammonium nitrate were mixed together in suitable proportions, moistened with minimum amounts of water after additions of different proportions of magnesium sulphate, granulated to obtain a product in the size range 2-4 mm. and partially dried by keeping for sometime in an oven at 60°C under a vacuum of 20 inches of mercury. Total N, total P_2O_5, water-soluble P_2O_5 and citrate-insoluble P_2O_5 in the products were determined within one to two days and thereafter the products were kept for two months in well-stoppered glass bottles at room temperature. The phosphate analyses were then repeated.

The results show that magnesium sulphate retards the formation of both citrate-insoluble and water-insoluble phosphate (Table 1). The action of magnesium sulphate in retarding the transformation of water-soluble to water-insoluble phosphate, as in the present case, does not seem to have been reported before although the effect of this salt in minimizing the formation of citrate-insoluble phosphate from dicalcium phosphate was known in a different context. Thus, with the addition of 20 parts of magnesium sulphate per 100 parts of P_2O_5 in the mixture of superphosphate and calcium ammonium nitrate, water-soluble and citrate-insoluble P_2O_5 were found to be respectively 44.91 and 2.12 per cent of the total, even after two months; when no magnesium sulphate was added the water-soluble and citrate-insoluble P_2O_5 were respectively 12.80 and 29.25 per cent after the same period.

According to the present thinking, a water-soluble

TABLE 1—ANALYSES OF CALCIUM AMMONIUM NITRATE—SUPERPHOSPHATE MIXTURES

Nos.	Mg SO_4, g./ 100 g. of P_2O_5	Total N, %	Total P_2O_5, %	Water-soluble P_2O_5, % of Total		Citrate-soluble P_2O_5, % of Total		Citrate-insoluble P_2O_5, % of Total	
				Fresh	After 2 Months	Fresh	After 2 Months	Fresh	After 2 Months
1.	0	6.15	16.07	16.82	12.82	66.17	57.87	17.01	29.31
2.	4	6.40	17.50	18.40	14.18	64.68	60.52	16.92	25.20
3.	8	6.35	17.13	21.66	15.65	61.53	60.71	16.81	23.64
4.	12	5,73	16.93	38.40	22.26	59.49	54.64	2.11	23.10
5.	16	5.85	16.46	49.58	36.52	48.37	61.36	2.05	2.12
6.	20	5.93	16.14	56.62	44.91	41.27	52.97	2.11	2.12

P_2O_5 amounting to over forty per cent of the total is generally not necessary for a phosphatic fertilizer. It would thus appear that addition of magnesium sulphate to the superphosphate-calcium ammonium nitrate mixture could make it an acceptable product, at least upto a period of two months after the preparation of the mixture.

Further studies are being continued with other proportions of superphosphate and calcium ammonium nitrate, and also on the effect of storage for a longer period on the properties of the mixtures.

The authors wish to thank Dr. K. R. Chakravorty, General Manager, for his interest in this work.

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A New Fungus from Rice Field Soils

By

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A new species of *Humicola* has been described. This is close to *H. Grisea* Traaen but differs in having much larger aleuriospores with thin walls.

In course of a study on the ecology of soil fungi, an interesting isolate (Culture No. 13) was obtained from a rice field of Falta in West Bengal. An account of its numerical abundance and some aspects of ecology has been reported[1]. As the cultural studies revealed some interesting taxonomical features, subcultures were referred to the Commonwealth Mycological Institute, Kew, England. Mr. Elphick of the same Institute studied the culture and opined that the fungus, belonging to the genus *Humicola*, may be a new species[2].

Humicola Oryzae Sp. Nov. (Fig. 1)

The fungus (IMI 94875) was isolated many times from roots of paddy plants but only rarely from soils.

Colony on 1.5 per cent malt agar fairly spreading but sparse with little or no aerial mycelium especially in young cultures; greenish black with zones of deeper and lighter shades; in older cultures some hyphal tips may protrude above the agar surface and these along with some trailing hyphae may give the surface a whitish appearance; reverse greenish black to black. *Hyphae* coarse, 1.75-5.5 μ, thick-walled, smooth, branched, septate, flexuous, mainly submerged and colourless with globular cell inclusions; some trailing along the agar surface may be light brown to dark with homogeneous contents. Branches are slightly constricted at the point of origin. *Aleuriophores* undifferentiated, colourless or lightly coloured, may

Humicola Oryzae

(a) Young aleuriospores showing globular contents, ×250
(b) mature aleuriospores with contents indistinguishable, ×200
(c) phialospores in heads and chains, ×500

be dilated towards the tips unbranched and separate 5-40μ long and 3-6μ wide excluding the swollen portions. *Aleuriospores* 14.3×14.9-22.2×23.0μ (average of 20 19.2×19.9μ) borne singly at the tip, smoky brown to black with globular contents (Fig. 1, a) which, however, become indistinguishable in mature black spores (Fig. 1, b). These are generally globose but may be ellipsoidal to pyriform occasionally. Cell wall uniformly thin showing double contour in young spores but not in mature ones. A few apical cells of the aleuriophores may be swollen, rounded and dark coloured, looking more or less like secondary aleuriospores. *Phialospores* 3-4×2-2.5μ were found in young cultures (5-7 days) on potato dextrose agar only. These are formed mainly on submerged phialides and rarely on aerial ones, borne in heads, but chains were also noted.

Coloniae in 1.5 per cent agaro maltoto patentes, sed sparsae, mycelio aereo in culturis recentibus exiguo vel nullo, viridinigrae, zonis coloris altioris et pallidioris alternantibus. In culturis maturioribus nonnulli hypharum apices protruduntur supra agari superficiem qui simul cum hyphis nonnullis repentibus coloniam albidam reddunt; facies versa viridinigra vel simpliciter nigra.

Hyphae crassae, furcatae, septatae et flexuosae, vulgo submersae et hyalinae, cellularibus inclusionibus globosis; nonnullae vero repentes per superficiem, pallide brunneae vel fuscae, contentis homogeneis. Ramuli aliquantum constricti ad punctum originis, crassis parietibus, leves, 1.75 ad 5.5μ lati.

Aleuriophora non differentiata, hyalina vel pallida, nonnumquam dilatata ad apicem, non ramosa sed septata, 5 ad 40 μ longa 3 ad 6 μ lata. Aleuriosporae 14.3×14.9 ad 22.2×23.0 (average 19.2×19.9μ) singulae insidentes singulis apicibus, fuliginosae vel nigrae, contentis; globosis quae in spora matura nigra indistincta, evadunt. Sporae vulgo vel globosae, vel ellipticae, vel pyriformes; parietes tenues, monstrantes Aleuriophori cellula apicalis una vel duplex tumescens, rotunda et fusca, aspectu aleuriosporarum secundariarum.

Phialosporae quoque notatae in culturis recentibus sed tantum in medio p.d.a., efformatae praesertim insidentes phialidibus submersis, nullibi aereis, vulgo capitulatae sed nonnumquam catenulatae, 3-4×2-2.5μ.

Holotypus, *A. C. Das—13*, lectus in radicibus maturis in oryzeto, positus in herbario mycologico, IMI 94875.

This isolate is close to *H. Grisea* Traaen but differs in having spores of much larger dimensions with a thin wall. A culture of *H.grisea* was obtained from the Central Bureau voor Schimmelcultures, Baarn, Netherlands, and a comparison is given below in order to bring out points of difference. 1.5 per cent malt agar was used.

	Humicola Oryzae	*Humicola Grisea*
Colony	Spreading rapidly (9 cm. in 5 days) but spares with little or no aerial mycellia.	Growth slow (4 cm in 5 days but forming heavy fairly compact aerial mat
Hyphae	Coarse, colourless or coloured, breadth 1.5-5.5μ	Fine, rather uniform, 2-3.5μ
Aleuriospores	Smooth, thin-walled, smoky brown to black, may range from 14.3×14.9 to 22.2×23.0μ average, 19.2×19.9μ	Smooth, thick-walled, yellowish brown to dark brown, may range from 10.5×11.4 to 14.9×15.4μ, average 12.5×13.6μ
Cellulolytic ability	NIL	STRONG

The holotype, *A. C. Das—13*, isolated from mature paddy roots of the cultivar Patnai-23 is preserved in culture under the same number at the Commonwealth Mycological Institute (IMI 94875); it was also isolated from soils of the same field.

Acknowledgements

The author's thanks are due to the Commonwealth Mycological Institute, Kew, England, and the Centraal bureau voor Schimmelcultures, Baarn, Netherlands for help in identification and valuable suggestions and to Rev. Father H. Santapau, Director, Botanical Survey of India, for rendering the Latin description. This is part of the research work carried out by the author during his tenure of Senior Research Fellowship under the C.S.I.R., Government of India, at the Bose Institute, Calcutta.

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Notes & News

Urea Synthesis

The Dutch State Mines have developed a new process for urea, which has many advantages over its predecessors such as (i) the power required per tonne of product is 120 KWh whereas the previous figures used to be 160-190 KWh, (ii) steam consumption is 1 tonne compared with 1.5-1.7/te urea and (iii) cooling water consumption is 55 m^3/te compared with 80-120 m^3/te for the older process.

A major feature is the ability to attain an ammonia efficiency of 90 per cent without a carbamate pump whereas previously 56 per cent was the best figure achieved. The recovery of the ammonia remaining in the solution leaving the synthesis recirculation unit permits the use of a much simpler pump, because the operating conditions are much milder.

The reaction takes place at 130-150 atm and 170-190°C, and the reaction mixture is stripped at synthesis pressure by CO_2 in a special design of stripper, which can be heated by indirect heat transfer from steam. At this stage the unconverted reactants are dissociated into CO_2 and NH_3 and recycled to the reactor along with fresh reactants. In the reactor the urea reaction follows the carbamate reaction, some of the exothermic heat being removed at this stage. The balance is removed in the carbamate condenser with the simultaneous generation of low pressure steam. The stripped urea solution, still containing small amounts of NH_3 and CO_2 is expanded and heated at about 1 atm in the case of partial recycle operation and 2-5 atm in the case of total recycle. The gases from the latter are passed to the carbamate condenser and the solution from it is recycled to the synthesis unit.

[Brit. Chem. Engng., **10** (1965), 749]

Ammoniation of Superphosphate

The presence of free acids in the superphosphate has the unfortunate effect of impairing in physical characteristics viz. its agglomerative and hygroscopic properties and at the same time causing corrosion of the production and handling equipment. These undesirable properties are generally eliminated by neutralising with ammonia or sodium carbonate.

In recent times the technology of ammoniation has reached a high pitch of development in TVA and elsewhere. A new type of ammoniation process having the special advantages of fluid bed technique has been developed by J. Trojan and V. Vanecek in Czechoslovakia [Brit. Chem. Engng., 10 (1965), 756]. Here ammoniation, granulation and product drying occur simultaneously. Ammoniation is carried out through absorption of gaseous ammonia present in a mixture with air, while the heat of reaction is sufficient to dry the product completely. The use of very low concentrations of gaseous ammonia eliminates completely the risk of degradation of the superphosphate through local overheating or through excessive ammonia uptake.

In a semi-production scale unit, the superphosphate is fed into the fluid bed reactor, the air for fluidising being fed by means of a blower situated beneath the grid of the reactor. A metered amount of ammonia is fed into the air stream before the latter is introduced into the reactor and the ammonia in the air is recovered in an absorber. The ammoniated superphosphate product is discharged through an overflow connexion in the reactor shell to a belt conveyor which transfers the product to a vibratory sieve which divides the product into three fractions; granules upto 2 mm., normal granules of 2 to 4 mm. and coarse materials. The latter fraction is treated in a disintegrator and returned to the superphosphate silo. The fluid bed mild-steel reactor is cylindrical, the part above the grid being of greater diameter than the grid and the transition being made through a conical section. The product is dried by air which is used for fluidisation and a greater part of the heat of evaporation is supplied by the reaction heat.

An increase in the nitrogen content in the product (more than 3 per cent N) can be advantageously effected by spraying solutions of ammonium salts or urea directly upon the fluid bed. The heat required to evaporate any moisture can be provided by increasing the heat content of the fluidising air supply, an inlet temperature of about 80°C is most suitable.

The above process enables a wide range of industrial fertilizers, based upon superphosphate or triple superphosphate to be produced. The use of gas mixture of ammonia/air allows the product to be dried through reaction heat; the efficiency of NH_3 absorption is extremely high and therefore eliminates the need for recovering NH_3 from the gases leaving the reactor.

Development in UAR's Fertilizer Industry

According to its Second Five Year Plan (1965-70), Egypt will more than double the current nitrogen fertilizer production capacity to about 450,000 tpa N by 1970. During this period high concentration materials, like urea, triple superphosphate (TSP) etc. will be introduced.

The Second Plan envisages a urea plant from coke oven gas with a capacity of 95,000 tpa at Helwan, where ammonia, nitric acid and CAN are presently produced. Carbon dioxide will be obtained from the CO_2 scrubbing system in the synthesis gas preparation plant. Urea will be produced by the partial recycle process, the off-gases being used in the manufacture of CAN. At the same time it is intended to complete the installation of three lines of production of CAN, each having a capacity of 200,000 tpa product.

A new 200,000 tpa ammonium sulphate plant at the fertilizer complex at Attaka, near Suez, where calcium nitrate and ammonium sulphate are already under production, is to be built using naphtha as feedstock.

At Aswan, a phosphorus complex based on phosphate rock from the Nile Valley will be established. Elemental phosphorus will be produced in an electric furnace at 25 tpd for conversion to phosphoric acid. The acid will be used to produce 25,000 tpa of TSP, 8,000 tpa of sodium tripolyphosphate. A 12,000 tpa feed-grade dicalcium phosphate plant is also to be erected at Aswan.

At Abu Zabal, where superphosphate is produced, a 40,000 tpa sulphuric acid plant is to be built.

With these developments a complete plant for the manufacture of 20 million 50 kg capacity plastic sacks each year will replace imported jute sacks.

[Nitrogen, No. 37 (1965), 20]

Granular Fertilizer Process

Scottish Agricultural Industries' above process reflects the growing tendency for superphosphate to be based upon other products derived from phosphoric acid. The main reason for the trend is the need for compound fertilizers of increased concentration with the ammonium sulphate ingredient replaced by ammonium nitrate.

In the new process, the differences in physical and chemical properties from the processing angle are quite considerable: the materials, softening at lower temperatures, are a great deal more hygroscopic and form a surface skin which inhibits moisture release. Ammonium nitrate, in particular, is far more hygroscopic than the sulphate, is less stable, being prone to decompose even in the absence of air above 150°C. Such conditions require the development of a special technique of granulation, e.g. it must be carried out at controlled temperatures and moisture levels in order to avoid overgranulation by a layering process. The process fulfils a number of other desirable conditions including elimination of hot spots and operation at low temperature and low moisture conditions.

The granulator has two concentric drums in which granular materials recirculates continuously. The solids pass along the outer drum into the inner drum and travel along it until they spill over the outer drum again. In the inner drum, where the air movement is restricted to what can pass through the free area at the feed chute, the introduction of phosphoric acid on the rapidly moving granular bed and injecting gaseous or liquid ammonia under the bed of acidified granules produces diammonium phosphate which acts as ammonia reservoir. Nitric acid is distributed and neutralised with ammonia on the bed in a similar manner at one end of the outer drum. The material then travels along the outer drum, into the inner drum and is dried before the cycle recommences. KCl is added here and is incorporated with the ammonium phosphate in the granule before coming to the nitric acid zone, a procedure which minimizes reaction with nitric acid.

Reaction, granulation and drying thus occur in a single unit, the drying being solely by chemical reaction, and the interval recirculating permits the direct addition of the acids, thereby eliminating separate reaction vessel.

[Brit. Chem. Engng., **10** (1965), 592]

News in Brief

Filtration of Fertilizer Liquors

In the ICI's new 300,000 tpa prilled ammonium nitrate plant at Severnside near Bristol, an automatically controlled precoat filtration system is an interesting feature. The end-product is known as Nitram, containing 34.5 per cent nitrogen. The filtration requirement is to produce, on a continuous basis, sufficient filtered solution to allow drawing from the stock tanks to proceed at a steady rate of 910 gph. The precoat is a 210 ft^3 stainless steel unit employing the patented 'ring pack' method comprising essentially a number of discs slipped over a fluted rod to provide a completely precoat support. This system of slurry feeding will be used and the cake is required to accommodate impurities and slurry feed present in a 4-hour cycle. The total required throughput of 3,640 gallons (4 gals at 910 gph) will be passed through the system in 3 hours in order to leave a generous 1 hour per cycle for cleaning and precoating.

All operations can be controlled from a programme console connected electrically to a valve chest in the filter house. The complete system comprises a 2,300 gals heated stainless steel reaction tank, a 1,500 gals slurry feed holding tank, a small (45 gals) media suspension metering tank, two heated filtered solution stainless steel stock tanks with a combined capacity of 22,000 gallons, control console, valve chest and all pumps and ancillary equipment.

[Brit. Chem. Engng., **10** (1965), 607]

Prilled Ammonium Nitrate

A superior product of ammonium nitrate containing 34 per cent N by dissolving 2 per cent of potassium nitrate as an additive has been developed by Southwest Potash Corpr. of USA. Melt temperatures were maintained in the range 350-380°F and prilling hole diameters 0.0292 to 0.045 inch were used. Potassium nitrate has the following effects: (i) lowers the transition temperature from form III to form IV crystals, (ii) it is possible to make form III the stable form throughout the ambient range of normal ambient temperatures, (iii) reduces the change in volume at the transition temperature and (iv) increases the critical humidity at the transition temperature, (v) changes in volume occur over a range of temperatures rather than at a single temperature, and (vi) reduces hygroscopicity. This kind of ammonium nitrate is superior to any commercial variety with respect to crushing strength and free flowing characteristics after temperature cycling twelve times between 70°-130°F.

[Nitrogen, No. 36 (1965), 35]

Analysis of Phosphate Fertilizers

DSM of Holland has developed an apparatus for determining automatically the phosphorus content of raw materials, intermediates and finished products in the phospnate fertilizer industry.

In this apparatus the solution is conveyed automatically to an automatic titration system where it is titrated with sodium hydroxide solution. The phosphoric acid present is neutralized and monosodium orthophosphate formed. Cerium III-nitrate solution is then added automatically, cerium III-phosphate is precipitated and two hydrogen ions liberated from each molecule of mono-phosphate. As a result, the solution again becomes acidic and it is neutralized a second time by adding more sodium hydroxide solution. The total quantity of sodium hydroxide solution consumed in the two titrations is a measure of the phosphorus content of the original sample.

As the precipitated cerium III-phosphate deteriorates rapidly, the glass electrode used in determining the end-point is rinsed automatically with hydrochloric acid after each titration.

[ECN, **8** (1965), 199, 40]

Large Phosphate Plant in Morocco

One of the largest fertilizer production plants, known as Safi Chemical Complex, has been put into operation in May 1965 by a Moroccan State organization. Designed by Krebs & Cie of Paris for the purpose of treating rock phosphate from Youssoufia deposits, the installation comprises 4 phosphoric acid production units each having a capacity 115 tonnes/day P_2O_5 utilizing the original single tank process of Pechiney-St Gobain-Union Chemique Belge and 2 triple superphosphate production units each having 600 tonnes/day capacity. One of these units is equipped for production of 18-48-0 ammonium phosphate.

Rock phosphate is treated in a 280 cu.m. reactor equipped with 2 helicoidal stirrer. Fumes and vapour produced are sucked out by a blower. Phosphoric acid and gypsum sludge are pumped out by a submerged pump and the separator of gypsum crystals from the acid is effected in a Prayon vacuum filter. Phosphoric acid of 30 per cent P_2O_5 is pumped to storage. The concentration plant can produce either 42 per cent P_2O_5 for the production of ammonium phosphate or 35 per cent P_2O_5 to increase the capacity of units producing triple superphosphate.

[Phosphorus & Potassium, No. 17 (1965), 23]

Phosphate Substitution in Calcium Sulphate

In the wet process of manufacturing phosphoric acid, one of the kinds of P_2O_5 loss is that it is incorporated in the calcium sulphate crystal and is not leachable.

The reason for this kind of loss is that HPO_4^{2-} ions which have very nearly the same geometric dimensions as the SO_4^{2-} ions, substitute them in the calcium sulphate lattice.

Increase of P_2O_5 content of the mother liquor or the presence of some foreign ions, such as ferric ions, increases the HPO_4^{2-} concentration and thus the substitutions. Increase of temperature which lowers viscosity, sulphuric acid excess, increasing content of solids in the suspension, increase of dosage or intensity of agitation decreases the substitution. A change resulting in an increased substitution is normally accompanied by a deterioration of the crystallization conditions.

[S. E. Dahlgren, Brit. Chem. Engng., **10** (1965), 776]

STATISTICS

TABLE 1—EUROPEAN FERTILIZER PRICES

N%	P_2O_5 total	P_2O_5 Sol	K_2O	Fertilizer	Grade	Basis	Packing	Minimum quantity	Price Local	Price Cent/lb
(1)	(2)		(3)	(4)	(5)	(6)	(7)	(8)	(9)	
				FRANCE					F/kg	
17.0	17.0	—	17.0	Compound fertilizer	—	Delivered farm Gironde-Languedoc	Bulk ..	20 tons	51.98	4.81
—	18.0	—	—	Basic slag	—	Ex depot Thionville including tax	50 kg paper sacks	20 ,,	8.798	0.81
—	—	18.00*	—	Single superphosphate	—	Free Mediterranean Zone excluding tax	Bulk ..	20 ,,	12.47	1.16
—	—	45.00*	—	Triple superphosphate	—	Ex Mediterranean port excluding tax	Bulk ..	20 ,,	33.00	3.05
46.0	—	—	—	Urea ..	Prilled	Delivered farm excluding tax	Bulk ..	20 ,,	46.20	4.28
18.0	46.0	—	—	Ammonium phosphate	—	Delivered farm Gironde-Languedoc	Bulk ..	20 ,,	58.95	5.46
33.5	—	—	—	Ammonium nitrate	—	Delivered farm excluding tax	Bulk ..	20 ,,	33.30	3.08
—	—	—	60.0	Potassium chloride	—	Delivered farm excluding tax	Bulk ..	20 ,,	20.421	1.89
				WEST GERMANY					DM/kg	
15.0	15.0	—	15.0	Compound fertilizer	Gelb	Free station	50 kg paper sacks	20 tons	32.25	3.66
10.0	15.0	—	20.0	Compound fertilizer	Violett	Free station	50 kg paper sacks	20 ,,	30.75	3.49
13.0	13.0	—	21.0	Compound fertilizer	Rot	Free station	50 kg paper sacks	20 ,,	32.25	3.66
10.0	8.0	—	18.0	Compound fertilizer	Grau	Free station	50 kg paper sacks	20 ,,	24.75	2.81
12.0	12.0	—	17.0	Compound fertilizer with boron	Blau extra	Free station	50 kg paper sacks	20 ,,	32.55	3.69
—	—	16.0*	—	Basic slag	—	Free Aachen	50 kg paper sacks	—	7.04	0.80
—	18.0	16.2	—	Single superphosphate	Prilled	Free station	50 kg paper sacks	20 ,,	16.39	1.86
26.0	—	—	—	Ammonium sulphate nitrate	—	Free station	50 kg paper sacks	20 ,,	28.54	3.24
21.0	—	—	—	Ammonium sulphate	—	Free station	50 kg paper sacks	20 ,,	22.71	2.58
22.0	—	—	—	Calcium ammonium nitrate	—	Free station	50 kg paper sacks	20 ,,	23.72	2.69
				HOLLAND					F/Kg	
12.0	10.0	—	18.0	Compound fertilizer	—	Delivered farm	Sacks	20 ,,	31.20	3.93
18.0	—	—	—	Single superphosphate	—	Delivered farm	Sacks	20 ,,	13.30	1.68
23.0	—	—	—	Calcium Ammonium nitrate	—	Delivered farm	Bulk	20 ,,	19.60	2.47

TABLE 1 —EUROPEAN FERTILIZER PRICES—*Contd.*

N%	P_2O_5 total	P_2O_5 Sol	K_2O	Fertilizer	Grade	Basis	Packing	Minimum quantity	Price Local	Price Cent/lb
(1)	(2)		(3)	(4)	(5)	(6)	(7)	(8)	(9)	
20.0	—	—	—	Magnesamon	10% MgO	Delivered farm	Sacks	20 „	21.70	2.73
—	—	—	—	Calcium nitrate	Flakes	Delivered wholesaler	Sacks	20 „	15.40	19.40
—	—	—	—	Calcium nitrate	Prilled	Delivered farm	Sacks	20 „	17.50	2.21
—	—	—	—	Potassium sulphate	Patent Kali	Delivered farm	Sacks	20 „	15.50	1.96
—	—	—	—	Ammonium sulphate	—	Delivered wholesaler	Bulk	20 „	15.90	2.01
				UNITED KINGDOM (England and Wales only)					£/long ton £. s. d.	
13.0	13.0	12.3	20.0	Compound fertilizer	High K51	Delivered farm	112 lb plastic sacks	6 „	23 6 11	2.94
20.0	10.0	9.3	10.0	Compound fertilizer	High N52	Delivered farm	112 lb plastic sacks	6 „	22 15 1	2.85
15.0	15.0	14.3	15.0	Compound fertilizer	High standard 54	Delivered farm	112 lb plastic sacks	6 „	24 14 3	3.09
8.0	20.0	18.8	16.0	Compound fertilizer	Low N55	Delivered farm	112 lb plastic sacks	6 „	22 2 10	2.76
—	—	—	—	Compound fertilizer with boron	High K51 plus boron	Delivered farm	112 lb plastic sacks	6 „	26 16 11	3.36
—	15.0	13.5*	—	Basic slag	—	Delivered farm	112 lb paper sacks	8 „	5 5 9	0.66
—	47.0	—	—	Triple superphosphate	Granular	Delivered farm	112 lb paper sacks	6 „	23 12 0	2.95
—	19.0	—	—	Single superphosphate	Granular	Delivered farm	112 lb paper sacks	6 „	10 5 0	1.28
—	—	—	60.0	Potassium chloride	—	Free on lorry	112 lb paper sacks	6 „	20 19 0	2.62
21.0	—	—	—	Ammonium sulphate	—	Delivered farm	112 lb paper sacks	6 „	13 6 0	1.66
—	—	—	50.0	Potassium sulphate	—	Free on lorry	112 lb paper sacks	6 „	23 2 6	2.89
—	—	—	—	Ammonium sulphate nitrate	—	Delivered farm	112 lb plastic sacks	6 „	18 7 10	2.30

[ECN 8 (1965), 199, 22]

TABLE 2—WORLD AMMONIA CAPACITY, M. TONNES N

	1963/64	1964/65	1965/66	Increase M. tonnes N	Increase %
Western Europe	6.53	7.41	8.25	0.84	15.4
Eastern Europe	3.73	4.65	5.86	1.21	26.0
Asia & Oceania	2.97	3.31	3.94	0.63	19.0
North America	6.01	6.87	8.82	1.95	28.5
Central and South America	0.51	0.66	0.67	0.01	1.5
Africa	0.32	0.32	0.89	0.07	22.0
	20.07	23.22	27.93	4.71	20.3

[Nitrogen, No. 37, (1965), 1]

TABLE 3—IMPORTS OF POTASSIC FERTILIZERS IN INDIA DURING JULY 1964 TO JUNE 1965, METRIC TONNES

Country from which imported	Muriate of Potash[1] 60% K_2O	Muriate of Potash[1] 50% K_2O	Sulphate of Potash[2] 50% K_2O
Belgium	—	—	506
France	10,000	—	2,066
Germany East	49,757	16,964	—
Germany West	14.047	—	1,076
Italy	—	—	5,176
Total:	73,804	16,964	8,824

Source: (1) Indian Potash Supply Agency Ltd., Madras.
(2) Monthly Statistics of the Foreign Trade of India.

[FAI Inf. Serv., 6 (1965), 20, 10]

TABLE 4—DISTRIBUTION OF NITROGENOUS POOL FERTILIZERS DURING 1964-65 (APRIL-MARCH), METRIC TONNES

State	*Ammonium Sulphate*	*Urea*	*Ammonium Sulphate Nitrate*	*Calcium Ammonium Nitrate*
Andhra Pradesh	106,250	49,413	9,544	77,850
Assam	4,612	154	—	100
Bihar	34,987	10,653	710	11,585
Gujarat	43,370	15,474	4,056	13,112
Jammu & Kashmir	5,420	—	—	2,718
Kerala	19,188	5,327	119	9,806
Madhya Pradesh	43,322	10,214	—	14,530
Madras	90,683	79,806	4,827	12,502
Maharashtra	111,283	41,167	8,488	13,083
Mysore	49,653	29,366	2,284	14,200
Orissa	8,214	14	—	27,326
Punjab	16,984	—	—	221,626
Rajasthan	7,576	2,069	873	23,640
Uttar Pradesh	65,542	8,984	14,396	97,937
West Bengal	65,899	9,482	422	2,639
Delhi	223	20	—	967
Goa	1,823	—	—	120
Himachal Pradesh	206	22	—	4,294
Manipur	239	64	—	441
Pondicherry	749	450	60	—
Tripura	—	10	—	845
Coffee Board	18,432	3,162	1,403	4,385
U.P.A.S.I.	25,263	454	—	—
Rubber Board	2,997	—	140	—
Tea (N. E. India)	72,311	—	—	—
Industrial Areas	1,500	1,772	—	—
Nepal	486	10	—	—
Miscellaneous	—	—	—	—
Total:	797,212	268,087	47,320	558,091

[FAI Inf. Serv., 6 (1965), 14, 10]

TABLE 5—IMPORTS OF NITROGENOUS FERTILIZERS IN INDIA DURING JULY 1964 TO JUNE1965, METRIC TONNES

Articles & Country from which imported		
Ammonium Sulphate[1]		
Germany East	..	39,000
Italy	..	29,000
Switzerland	..	7,484
United Kingdom	..	39,933
U.S.A.	..	350,365
U.S.S.R.	..	17,685
Western European countries	..	85,200
Total:	..	568,667
Urea[1]		
Norway	..	8,000
Mexico	..	10,007
Japan	..	145,400
Western European countries	..	122,089
Total:	..	285,496
Chilean Natural Nitrate of Soda[2]		
Chile*	..	6,000
Total:	..	6,000
Ammonium Chloride[1]		
Japan	..	2,000
Total:	..	2,000
Other Nitrogenous Fertilizers[1]	..	
Austria	..	3,744
France	..	6,720
Germany West	..	4,649
Poland	..	3,016
United Kingdom	..	9,046
Total:	..	27,175

* For Agricultural purposes only.

Source: 1. Ministry of Food & Agriculture, New Delhi.
2. Rallis India Ltd., Bombay.

[FAI Inf. Serv., 6 (1965), 23, 10]

TABLE 6—PRODUCTION & CONSUMPTION OF FERTILIZERS IN INDIA, METRIC TONNES

Production					*Consumption*				
Fertilizer	1961-62	1962-63	1963-64	1964-65	*Fertilizer*	1961-62	1962-63	1963-64	1964-65
Ammonium Sulphate	402,303	433,132	429,156	441,000	Ammonium Sulphate	792,404	811,582	821,444	1,025,000
Ammonium Sulphate Nitrate	53,194	58,304	47,252	46,000	Ammonium Sulphate Nitrate	80,063	59,628	36,950	56,500
Urea	13,535	18,698	18,911	18,000	Urea	155,634	167,948	262,461	315,000
Calcium Ammonium Nitrate	228,109	370,829	496,349	605,000	Calcium Ammonium Nitrate	238,166	290,257	541,246	620,000
Ammonium Chloride†	11,156	13,834	13,720	16,000	Ammonium Chloride†	8,351	6,699	13,411	17,000
					Nitrophosphate	5,000	15,246	19,000	33,000
Superphosphate (16% P_2O_5)	391,969	535,434	623,929	829,000	Chilean Nitrate of Soda (natural)	8,403	12,560	6,165	7,400
Superphosphate (18% P_2O_5)	—	—	7,643	8,000	Superphosphate (16% P_2O_5)	380,490	512,691	646,079	800,000
Superphosphate (19% P_2O_5)	—	—	2,816	—	Superphosphate (18% P_2O_5)	—	—	903	700
					Superphosphate (19% P_2O_5)	—	—	185	—
Ammonium Phosphate Sulphate (16-20-0)	13,223	13,156	30,481	60,000	Ammonium Phosphate Sulphate				
					16-20-0	10,282	12,164	30,756	41,600
					20-20-0	—	23,646	44,483	48,200
					Potassium Nitrate	45,616	63,649	81,630	99,000
					Potassium Sulphate	6,146	3,502	5,816	6,500

* Estimated
† For agricultural use

[Production & Consumption of Fertilizer, Annual Review 1964-65 (Fertilizer Assn. of India, New Delhi), Aug. 1965]

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